

VOL. XIV. 2.

JULY, 1861.

THE
QUARTERLY
JOURNAL
OF
THE CHEMICAL SOCIETY.

Committee of Publication.

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Nº LIV.

LONDON:

HIPPOLYTE BAILLIERE, 219, REGENT STREET,
and 440, BROADWAY, NEW YORK.

PARIS: J. B. BAILLIERE, LIBRAIRE, RUE HAUTEFEUILLE.

MADRID: BAILLY BAILLIERE, LIBRAIRE, CALLE DEL PRINCIPE.

1861.

Price Three Shillings.

LONDON: PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W. C.

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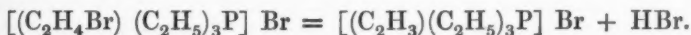
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phosphonium-salt simply by the elements of one molecule of water, which the latter contains less, the question naturally suggested itself whether, under the influence of heat, the oxethylated compound might not be converted into the vinyl-body. The results of two experiments appear to answer this question in the affirmative. In one case, the bromide of bromethyl-triethylphosphonium had been boiled for a considerable time with oxide of silver. In another experiment, a concentrated solution of the oxethylated base was evaporated over an open flame until a very appreciable quantity was entirely decomposed. In both cases, it was proved by analysis that the oxethylated base had been transformed into the vinylated compound. In a third experiment, however, in which the temperature was not allowed to rise above 150° , the oxethylated compound was not altered.

The vinyl-compound appears to be formed also by the action of heat upon the bromethylated bromide:



Torrents of hydrobromic acid are evolved, and the residue yields, after treatment with chloride of silver, on addition of dichloride, an octohedral platinum-salt. The decomposition is, however, completed only with difficulty. The evolution of hydrobromic acid continues for hours, even when the salt is kept at a temperature (between 235° and 250°), at which considerable quantities are entirely decomposed. I have thus been prevented from procuring an amount of the salt sufficient for its identification with the vinyl-compound obtained by the action of acetate of silver.

Vinyl-triethylphosphonium-salts are formed in one or two other reactions, which will be noticed in subsequent paragraphs of this inquiry.

SERIES OF DIATOMIC COMPOUNDS. DIPHOSPHONIUM COMPOUNDS.

Salts of Ethylene-hexethyl-diphosphonium.

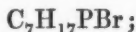
Dibromide.—The occurrence of this salt among the products of the action of dibromide of ethylene on triethylphosphine has already been mentioned in the introduction to the experimental part of the memoir. On bringing together the materials in the proportions indicated by the equation



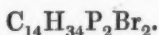
that is to say, one volume of dibromide of ethylene and three volumes of the phosphorus-base, the diatomic compound is obtained, nearly in the theoretical quantity. It is distinguished

from the monatomic product of the same reaction by its much greater solubility even in absolute alcohol, from which it separates only after almost complete evaporation, in needles which are permanent in the air. In ether this salt is insoluble, as are in fact most of the bromides of the phosphorus-bases, both monatomic and diatomic. The dibromide obtained by the direct action of dibromide of ethylene on triethylphosphine, always contains a small quantity of the monatomic bromide, from which it can only be purified with great difficulty. And further, if the dibromide of ethylene has not been carefully purified from adhering hydrobromic acid, the resulting salt is likewise contaminated with traces of the extremely soluble hydrobromate of the phosphorus-base, the presence of which likewise interferes very much with the purification of the product. Lastly, the formation of oxide of triethylphosphine can never be entirely avoided, even when the operation is conducted in an atmosphere of carbonic acid. To obviate these inconveniences, the compound submitted to analysis was prepared by saturating the hydrate, to be presently described, with hydrobromic acid.

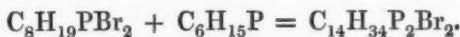
The simplest expression of the results obtained in the analysis of this compound is the formula



its formation, however, and its, deportment, fully to be discussed in the following paragraphs, prove unmistakeably that this expression must be doubled, and that the weight and composition of the molecule of this body is represented by the formula



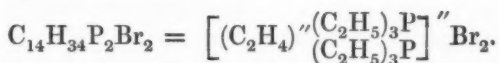
On comparing the composition of the two bromides which are formed from dibromide of ethylene by the fixation of one or two molecules of triethylphosphine, it could scarcely be doubted that the monatomic compound, even when already formed, must still be in a condition to take up the second molecule of triethylphosphine, and thus to pass into the diatomic bromide. The correctness of this supposition is easily established by experiment. The monatomic bromide acts strongly, even at ordinary temperatures, on a fresh quantity of the phosphorus-base, being transformed, with evolution of heat, into the diatomic compound,



In presence of alcohol and at 100° , the reaction is completed in a few seconds. With lively interest have I followed up the result of this simple experiment: for its success obviously pointed to a source from which an almost incalculable number of diatomic compounds of the most varied composition might be obtained.

For this reason I have not omitted to establish by numbers the conversion of the monatomic into the diatomic bromide, and in the following sections I shall have frequent occasion to quote results, which leave no doubt as to the facility of this transformation.

The molecular constitution of the new bromide is satisfactorily represented by the formula

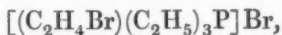


The salt is derived from a diatomic metal, a diphosphonium, in which 6 equivs. of hydrogen are replaced by 6 equivs. of ethyl, and the remaining 2 equivs. of hydrogen by the radical ethylene indivisible under the given circumstances. It is the diatomic character of the ethylene that links together the two molecules of triethylphosphine, and gives to the new molecular system the necessary stability.

The dibromide is very easily attacked by silver-compounds, and in this manner an extensive series of very sharply characterized diphosphonium-salts may be obtained, many of which crystallize remarkably well. In these reactions, however, a tendency towards the formation of double compounds is frequently observed, and hence it is for the most part better to prepare the salts by treating the free base with the corresponding acids.

In examining the dibromide, I have made some observations which I may take an opportunity of pursuing further by and by. When the aqueous solution of this salt is mixed with bromine-water, very beautiful yellow needles are immediately separated, consisting of a polybromide. These needles may be recrystallized from boiling water, but apparently not without decomposition. They have but an ephemeral stability. On boiling the compound, bromine continues to be evolved, and ultimately the original bromide is left behind. Polybromides of exactly similar character are formed by the action of bromine on the bromides of all the ammonium- and phosphonium-bases that I have examined.

I have already pointed out that, in fixing one molecule of triethylphosphine to form the compound



dibromide of ethylene exhibits a deportment which might have been expected from bromide of bromethyl, with which it is isomeric. It was of some interest to examine experimentally, the behaviour of triethylphosphine with monobrominated bromide of ethyl. This substance had never been prepared. I have obtained it, together with the dibrominated bromide of ethyl $(\text{C}_2\text{H}_3\text{Br}_2)\text{Br}$, by submitting bromide of ethyl to the action of dry bromine under pressure at a temperature of 180°C . Brominated bromide

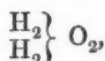
of ethyl is a heavy aromatic oil, boiling at 110° C., and consequently differing altogether from dibromide of ethylene, which boils at 130° C., and with which it is isomeric. The brominated bromide attacks the phosphorus-base much more slowly than the dibromide; the final result, however, is exactly the same, the bromide of the bromethylated monophosphonium and the dibromide of the ethylene-diphosphonium being produced. The former of these salts is obtained in comparatively small quantity, and I was therefore unable to identify the compound in question with the bromethylated bromide obtained by means of the ethylene-compound, otherwise than by the characteristic reaction with silver-salts, mentioned in an earlier paragraph of this paper. The diphosphonium-compound, on the other hand, is easily produced in sufficiently large quantity, by means of brominated bromide of ethyl. I had no difficulty in establishing the absolute identity of this compound with the product obtained from dibromide of ethylene, by a careful comparison of the chemical and physical properties of the substances, and moreover by the analysis of a di-iodide and a platinum-salt derived from the bromide-of-ethyl-derivative.

Dihydrate.—The free base is easily obtained by the action of oxide of silver on the dibromide, or better on the di-iodide, which latter is, of all the diphosphonium-compounds of this class, the easiest to obtain in the pure state. If the alcoholic solution of the crude dibromide be used in this experiment, the first portions of oxide of silver added to the liquid are completely dissolved, and the solution, which has already become alkaline, deposits a white crystallized double compound of the dibromide with bromide of silver, which, however, is completely decomposed by further addition of oxide of silver and dilution with water. In this manner, there is produced an extremely caustic, nearly odourless liquid, having a strongly alkaline taste, and exhibiting the bitterness which is so often observed in the analogous bodies of the nitrogen-series. In other respects, the base exhibits the properties which characterize the hydrates of tetrethylphosphonium* and tetrethylammonium.† The solution, when evaporated in an open vessel, rapidly absorbs carbonic acid, and ultimately yields a semi-crystalline mixture of dihydrate and carbonate. When evaporated *in vacuo* over sulphuric acid, the caustic solution gradually dries up to a syrupy, extremely deliquescent mass, which exhibits no traces of crystallization. On mixing the highly concentrated solution of the dihydrate with solution of potassa, the base is separated from the liquid in oily drops, which are, however, readily dissolved on addition of water. The free base, like the corresponding monophosphonium- and even monammonium-

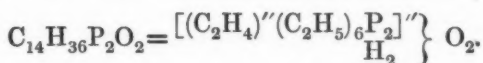
* Phil. Trans. 1857, Part II. p. 583. Chem. Soc. Qu. J. xi. 65.

† Phil. Trans. 1851, Part. II. p. 357. Chem. Soc. Qu. J. iv. 304.

compounds, cannot therefore be obtained in a state fit for analysis; its formation, however, as well as its conversion into a series of well-defined salts corresponding to the dibromide, characterize it as an oxide derived from the type,—



as the hydrated dioxide of ethylene-hexethyl-diphosphonium :



Complicated as the construction of this compound must appear, it is remarkable for its stability. The solution may be boiled and considerably concentrated upon the water-bath without decomposition, and remains unchanged even when exposed for some time under pressure to a temperature of 150° ; indeed the decomposition of the hydrate does not begin till the liquid is evaporated to dryness. The changes which this compound suffers under the influence of higher temperatures are not without interest. They are rather intricate, and I propose therefore to devote a special paragraph to their study.

In its deportment with metallic salts, the hydrate of the diphosphonium closely resembles the fixed alkalis, as may be seen from the following Table:—

Deportment of the Hydrate of Diphosphonium with reagents.

Barium-salts	} White precipitates of the hydrates.
Strontium-salts	
Calcium-salts	
Magnesium-salts	
Aluminium-salts	White precipitate of hydrate of aluminium, soluble in excess of the precipitant.
Chromium-salts	Green precipitate of hydrate of chromium, soluble in an excess of the precipitant, and reprecipitated on ebullition.
Nickel-salts . .	Apple-green precipitate of the hydrate.
Cobalt-Salts . .	Blue precipitate of the hydrate.
Iron-salts :—	
<i>Ferrosium</i> . .	Greenish precipitate of the hydrate.
<i>Ferricum</i> . .	Reddish-brown precipitate of the hydrate.
Zinc-salts . . .	White gelatinous precipitate of the hydrate, insoluble in excess.
Lead-salts . . .	White amorphous precipitate of hydrate of lead, soluble in excess.
Silver-salts . .	Black-brown precipitate of oxide of silver.
Mercury-salts :—	
<i>Mercurosum</i> .	Black precipitate of the suboxide.
<i>Mercuricum</i> .	Yellow precipitate of the oxide.
Copper-salts . .	Light blue precipitate of the hydrate, insoluble in excess: in presence of sugar, the precipitate dissolves in excess, forming an azure-blue solution, from which, if glucose has been employed a red precipitate of suboxide of copper separates on ebullition.
Cadmium-salts }	} White precipitates of the hydrates.
Bismuth salts }	

Tin-salts:

Stannosum :—

Chloride,
containing free
hydrochloric
acid White acicular precipitate of a double compound.

Stannicum :—

Chloride White gelatinous precipitate, extremely soluble in excess.

Antimony :—

Trichloride White acicular precipitate of a double compound.

Gold :—

Trichloride Golden-yellow crystalline precipitate of a double compound.

Platinum :—

Dichloride Pale-yellow, slightly crystalline precipitate of a double compound.

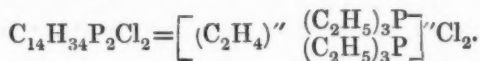
These are, with few exceptions, the reactions of a solution of potassa. It is scarcely necessary to add that the hydrate of the diphosphonium expels, even at the common temperature, ammonia, phenylamine, triethylphosphine, and a considerable number of other amines and phosphines from their saline combinations.

The free base exhibits the deportment of caustic potassa towards iodine and sulphur. It dissolves crystals of *iodine* with facility; the colourless solution is neutral, and yields on evaporation a syrup-like half-crystalline mass, easily recognized as a mixture of the di-iodide with the di-iodate. Treatment with alcohol separates the crystals of the more difficultly soluble iodide from the gummy iodate. On adding concentrated hydrochloric acid to the liquid obtained by dissolving iodine in the free base, a dark-coloured substance (iodine or a periodide) is separated; after a few seconds, however, the liquid is decolorized and solidifies to a mass of beautiful lemon-yellow crystals. The diphosphonium-salts are thus seen to exhibit phenomena exactly similar to those which were observed by Weltzien in the case of the compounds of tetramethyl- and tetrethyl-ammonium. I hope to find an opportunity of returning to a more minute examination of the yellow compound, which, by recrystallization from boiling alcohol, may be obtained in splendid needles, and which will probably be found to be a compound of the di-iodide with chloride of iodine. For the present I may remark that similar compounds are formed by all the bases of the type ammonium and diammonium which I have examined, provided they belong to that class in which the substitution is complete. A variety of monophosphonium- and mon-arsonium-salts, and lastly of compounds of phosphammoniums and phospharsoniums, submitted to the same process, have furnished perfectly similar results. Hydrochloric acid occasionally produces crystalline precipitates in the concentrated solutions of the iodates, even of bases of incomplete substitution; these precipitates disappear, however, on addition of water, or on gently warming, and are essentially different from the compounds previously mentioned. *Sulphur* dissolves in a concentrated solution of the dihydrate,

although with difficulty, to a yellow liquid, which precipitates the black sulphide from lead-solutions, and is decomposed by acids, with separation of sulphur and evolution of sulphuretted hydrogen. *Phosphorus* is not attacked by the solution of the dioxide, not a trace of phosphoretted hydrogen being evolved, even by protracted ebullition.

Disulphhydrate.—The solution of the base saturated with hydro-sulphuric acid, when allowed to remain for some time over sulphuric acid *in vacuo*, dries up to a gummy mass, which exhibits as little inclination to crystallize as the dihydrate itself. When evaporated on the water-bath in contact with the air, the disulphhydrate is decomposed, the sulphur being oxidized; ultimately an imperfect crystallization of the sulphate remains behind.

Dichloride.—This salt is easily obtained by treating the dibromide or the di-iodide with chloride of silver, and also by saturating the free base with hydrochloric acid; it is extremely soluble in water and in alcohol, insoluble in ether. The concentrated solution solidifies over sulphuric acid into a mass of large and highly deliquescent crystalline plates of a pearly lustre, which may be exposed to a very high temperature (290° to 300°) without the slightest alteration. The salt is precipitated unchanged from its aqueous solution by potassa; it contains—



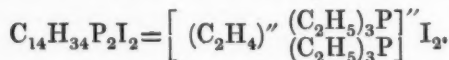
The dichloride forms with metallic chlorides numerous well crystallized double compounds, some of which will be more particularly described hereafter.

The dichloride of the ethylene-diphosphonium is likewise produced by the action of monochlorinated chloride of ethyl, prepared, in accordance with Regnault's indications, by the action of chlorine upon chloride of ethyl. The chlorinated compound acts but slowly upon triethylphosphine at 100°. By digesting for twenty-four hours at 120°, a considerable proportion solidified to a white fibrous crystalline mass, which proved to be exclusively the dichloride of the diphosphonium. It was identified by conversion into the characteristic platinum-salt, and subsequently into the iodide, both of which were analysed.

Di-iodide.—This salt is perhaps the most characteristic of the diphosphonium-compounds. Crystallizing with peculiar readiness,—being easily soluble in hot, but sparingly soluble in cold water,—slightly soluble also in alcohol, and insoluble in ether,—it possesses all the properties which can facilitate the preparation of a pure and definite substance. It has therefore, for the most part, served as a starting-point in the preparation of the diphosphonium-compounds.

I have already remarked that, in the preparation of the mona-

toxic bromide, the formation of the dibromide can scarcely ever be entirely prevented. The mother-liquors, remaining after numerous preparations of the monatomic bromide, were therefore united and treated with oxide of silver, whereby a caustic liquid was obtained, containing the hydrate of the diphosphonium, contaminated with the hydrate of the oxethylated monophosphonium arising from the decomposition of the bromethylated compound. These hydrates were converted, by saturation with hydriodic acid, into the corresponding iodides, the separation of which presented no further difficulty, inasmuch as the iodide of the oxethylated monophosphonium is extremely soluble in water and in alcohol. The sparingly soluble di-iodide was easily obtained in a state of perfect purity by several crystallizations. The crystals are anhydrous. Any hygroscopic moisture that may adhere to them is most conveniently removed by drying them over sulphuric acid, since the salt begins to turn slightly brown at 100° . Analysis proves this iodide to be represented by the formula,—



The di-iodide crystallizes from boiling water in needle-shaped crystals, which often attain a considerable size. Quintino Sella has communicated to me the following results, which he has obtained on examining these crystals:—

“ System trimetric :—

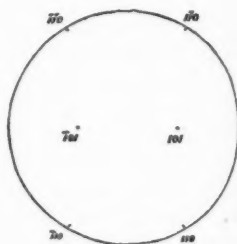
Fig. 41.

$$001, 101 = 45^{\circ} 9'$$

$$100, 110 = 60^{\circ} 18'$$

Forms observed :—

$$110, 101 \text{ (Fig. 41).}$$



$$\text{M M} = 119^{\circ} 40'; \quad b : h = 1 : 0.8732.$$

Forms observed :—

M é.

Combinations observed :—

110, 101 (Figs. 42, 43). 110, 101 with other faces, too much rounded for their correct determination (Fig. 44).

Fig. 42.

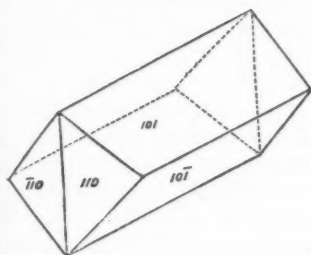


Fig. 43.

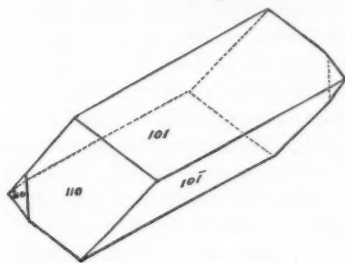
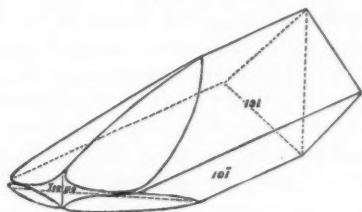


Fig. 44.



Cleavages 110 und 101 distinct, and easily obtained.

The crystals are long needles; the faces 110 are often but little developed (Fig. 43); they have then a monoclinic aspect; but the measurement of the angles 110 , 101 , and $\bar{1}10$, $\bar{1}01$, has furnished nearly the same result; and moreover, on examining the crystals with the polarizing microscope, the line $[010]$ is found to be nearly one of the axis of elasticity.

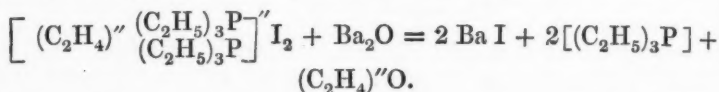
The angle 101 , $\bar{1}01$ is so near to 90° , that there might appear some reason for regarding the crystals as dimetric hemihedrals. I am not, however, of this opinion, for I have observed, only two cleavages, 110 , $\bar{1}10$, instead of the four corresponding to the dimetric system; moreover the angle 101 , $\bar{1}01$ has *always* been found a little greater than 90° .

The needles, when small, are transparent; the larger ones are rather milky, and hollow inside.

The lustre of the faces 101 is slightly nacreous, that of the faces 110 is vitreous."

The di-iodide, as already observed, is very much more soluble in boiling water than in cold water. 100 parts of boiling water dissolve 458.3 parts of the salt, of which only 3.08 parts remain in solution at 12° . A remarkable character of the salt is its insolubility in moderately concentrated solution of potassa; the dilute solution mixed with potassa immediately yields a crystalline precipitate; the same property is exhibited, as is well known, by the iodides of tetrethylammonium and of the other ammonium- and

phosphonium-metals. The solution of the di-iodide, like those of the diphosphonium-salts in general, is perfectly neutral; it is colourless when first prepared, but on exposure to light soon acquires a tint of yellow, and finally turns brown, at the same time depositing a reddish compound, doubtless analogous to the periodides, which, as I observed some time ago, are formed under similar circumstances from the iodides of tetramethyl- and tetrethyl-ammonium, and which have since been so successfully studied by Weltzien. This red compound is immediately precipitated on adding a solution of iodine to the colourless solution. The di-iodide, like most diphosphonium compounds, exhibits great stability. It melts, without the slightest decomposition, at 231° , and solidifies, with crystalline structure, a few degrees lower. When more strongly heated over an open flame it is decomposed, with formation of a red-brown substance, which I have not examined. On distilling the di-iodide with excess of caustic baryta in an atmosphere of hydrogen, triethylphosphine passes over: no gaseous product is formed in this reaction. Together with iodide of barium, which remains behind, and triethylphosphine which distils over, probably oxide of ethylene is formed in this reaction.



I should, however, state that I have not succeeded experimentally in tracing the formation of the oxide of ethylene.

An attempt to decompose the solution of the di-iodide with sodium-amalgam was unsuccessful; the salt, which is likewise but sparingly soluble in solution of soda, immediately separated out, and no appearances were observed which might have indicated the formation of the ammonium-amalgam. It is worthy of remark that no substituted ammonium-amalgam has yet been produced.

The di-iodide forms, with various metallic salts, crystalline double compounds, among which I have more particularly examined the zinc-salt; its analysis will be given further on.

Difluoride.—The solution of the hydrate, neutralized with hydrofluoric acid and dried over sulphuric acid, leaves a colourless transparent syrup, which does not crystallize, even after standing for a considerable length of time in air or *in vacuo*. The fluorine-compound, like the other diphosphonium-salts, is soluble in alcohol, but insoluble in ether.

Silico-fluoride.—The solution, neutralized with hydrofluosilicic acid, likewise failed to yield crystals by evaporation.

Dicyanide.—The solution of the hydrate, mixed with excess of hydrocyanic acid, retains its alkaline reaction; when evaporated on the water-bath, it gives off every trace of hydrocyanic acid. On digesting a solution of the di-iodide with excess of cyanide of

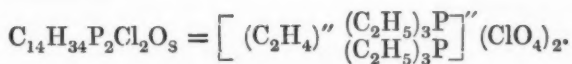
silver, a double compound dissolves, which crystallizes in splendid needles, but is likewise decomposed by evaporation, with evolution of hydrocyanic acid and separation of cyanide of silver.

Disulphocyanate.—When a solution of the di-iodide is boiled with excess of recently precipitated sulphocyanate of silver, a solution of the disulphocyanate is obtained, perfectly free from silver, and solidifying by evaporation on the water-bath into a crystalline mass. The salt dissolves readily in water and in alcohol, and is precipitated therefrom by ether. The aqueous solution is likewise precipitated by potassa, the oily drops thus separated gradually solidifying into crystalline rosettes.

Dinitrate.—This salt, prepared by saturating the base with nitric acid, forms laminar crystals, permanent in the air, extremely soluble in water, less soluble in alcohol, and precipitated from the alcoholic solution by ether, as an oil which gradually solidifies. The solution forms with mercuric chloride, a precipitate which crystallizes in needles.

Diperchlorate.—This salt is perhaps the most beautiful of the diphosphonium-compounds. On mixing moderately concentrated solutions of the hydrate and perchloric acid, the liquid is soon traversed by delicate crystalline needles, often an inch long. They may be recrystallized from boiling water and dried at 100° without decomposition. At a higher temperature, they are decomposed, with slight detonation.

The analysis of the diperchlorate, in which the diphosphonium was weighed in the form of the nearly insoluble platinum-salt, led to the formula:—



Di-iodate.—The base, neutralized with iodic acid and evaporated over sulphuric acid, yields an extremely deliquescent syrup which crystallizes but gradually. Solution of potassa separates the hydrate from the concentrated solution, in oily drops, sparingly soluble crystalline iodate of potassium being at the same time precipitated. The solution, mixed with hydrochloric acid, yields the lemon-yellow crystalline compound already mentioned.

Carbonate.—The solution of the oxide remains alkaline, even after saturation with carbonic acid; on evaporation, it leaves a mass having a slightly crystalline structure.

Sulphate.—Radio-crystalline, extremely deliquescent salt. Repeated attempts to produce diphosphonium-alums by mixing the solution with the sulphates of aluminium and chromium were unsuccessful.

Chromate.—The solution of the base, neutralized with pure chromic acid, deposits, when exposed to an atmosphere dried by sulphuric acid, extremely soluble needles arranged in stellated

groups. With excess of chromic acid, nothing but an uncrystallizable syrup is obtained.

Oxalate.—Both the acid and the neutral solution of the base in oxalic acid dries up to a slightly crystalline mass.

Phosphate.—The di-iodide, boiled with excess of phosphate of silver, yields a neutral solution of the phosphate of the diphosphonium, which remains as a slightly crystalline mass when the solution is evaporated. Crystallization is not promoted by addition either of free phosphoric acid or of the hydrate.

Tartrate.—Extremely soluble; difficult to crystallize.

Dipicrate.—The aqueous solution of picric acid, added to a moderately concentrated solution of the hydrate, instantly produces a yellow crystalline precipitate, which separates from the boiling alkaline solution in long needles.

The diphosphonium-salts form a long series of double compounds, most of which crystallize splendidly.

Platinum-salt.—The solution of the dichloride, even when extremely dilute, yields with dichloride of platinum a pale-yellow precipitate, which appears amorphous to ordinary observation, but when examined under a microscope of rather high power, resolves itself into small prisms. This salt is nearly insoluble in cold and even in boiling water, so that, as already observed, the diphosphonium may be quantitatively estimated in this form. The precipitate dissolves, though with difficulty, in concentrated hydrochloric acid, and crystallizes from the solution, by slow cooling, in small but well-defined crystals of a bright orange-red colour.

Quintino Sella has examined these crystals, and obtained the following results:—

“System monoclinic:—

$$100, 001 = 82^{\circ} 36'$$

Forms observed:

$$100, 010, 001 \text{ (Fig. 45).}$$

Fig. 45.

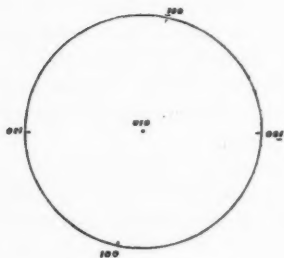
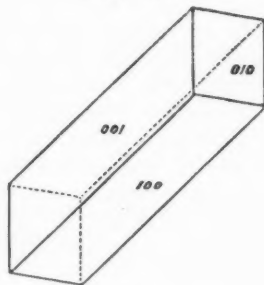


Fig. 46.



Combinations observed:—

$$100, 010, 001 \text{ (Fig. 46).}$$

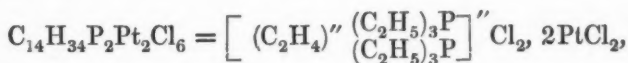
Cleavages 100, 010, 001 distinct and easily obtained, more especially 010.

The crystals are elongated in the direction of the axis of symmetry, and often hollowed out for a great part of their length when rather thick, that is to say, when their sides attain the width of half a millimetre. The hollow has the form of a pyramid having its base on the face 010 and its apex towards the centre of the crystal. The face 010 is often reduced to a very narrow rectangular rim. The opposite apex of the crystal is irregular, as if it had adhered to the side of the vessel. The face 001 is in general rather more developed than 100.

The crystals are optically negative. The plane of the optical axes is parallel to the line of symmetry [010]; the principal medium line is perpendicular to the latter and forms an angle of about 30° with a line normal on face 001. In fact, a plate parallel to 010 stops the passage of a ray of polarized light in that direction. Moreover, rings are observed through the faces 001 and in a plane parallel to the line of symmetry 010, and rather inclined towards a line normal on each face. The angle of the optical axis seen in this manner through the faces 001 appears to be very nearly 110° .

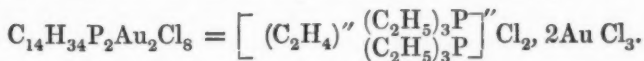
The crystals have a very fine orange-colour and a vitreous lustre."

This platinum salt by numerous analyses was found to contain:—



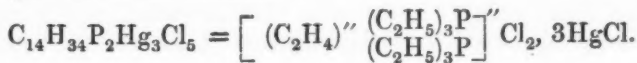
Palladium-salt.—A dilute solution of the dichloride is not precipitated by chloride of palladium. On concentrating the mixture and allowing it to cool slowly, reddish-yellow prisms make their appearance: by rapid evaporation a brick-red crystalline powder is obtained. Alcohol added to the aqueous solution of the two salts throws down the double salt as a chocolate-coloured crystalline magma composed of small interlaced needles. I have not analysed this compound.

Gold-salt.—Beautiful golden-yellow needles, difficultly soluble in cold, easily soluble in boiling water and containing

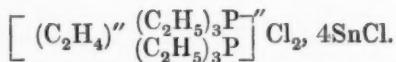


Mercury-salt.—Delicate crystalline needles or laminae sparingly soluble in water and in alcohol, obtained by mixing the chloride of the diphosphonium with mercuric chloride.

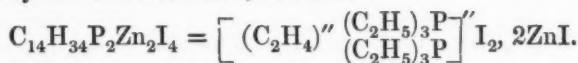
Analysis led to the formula



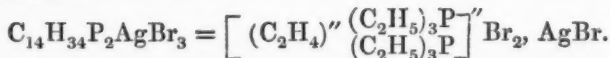
Tin-salt.—This salt, which is prepared like the mercury-compound, crystallizes from water in large well-formed prismatic crystals. According to some determinations, which, however gave only approximate results, the tin-salt appears to have the composition :



Di-iodide and Iodide of Zinc.—On mixing the two solutions, a crystalline precipitate is obtained, which separates in long needles when recrystallized from boiling water. The salt, which is apt to assume a yellowish coloration, contains



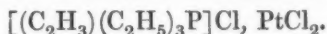
Dibromide and Bromide of Silver.—I have mentioned this salt already when describing the preparation of the hydrate from the dibromide. When oxide of silver, which should not be mixed with too much water, is added in small portions to a boiling concentrated solution of the dibromide in alcohol as long as it dissolves, the filtered solution deposits on cooling white crystals, which contain



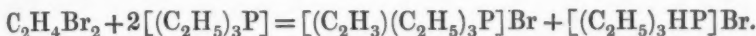
The salt crystallizes, but not readily, from boiling alcohol. It is immediately decomposed by water, bromide of silver being separated, and the bromide of the diphosphonium passing into the solution.

In describing the general character of the action of dibromide of ethylene upon triethylphosphine, I have mentioned that, in addition to the monatomic and diatomic bromides, which are the principal products of the reaction, secondary compounds may be formed, but always in comparatively small quantities. The mother-liquors generally contain oxide of triethylphosphine, formed by the action of the atmosphere ; they contain, moreover, bromide of triethylphosphonium, if the dibromide had not been carefully deprived of hydrobromic acid. The bromide of triethylphosphonium, however, under certain conditions, arises from the decomposition of dibromide of ethylene into hydrobromic acid and bromide of vinyl, the latter producing in this case the bromide of vinyl-triethylphosphonium. I had an opportunity of establishing this fact experimentally, when preparing a considerable quantity of the dibromide of the diphosphonium. The phosphorus-base having been employed in excess in this operation, not a trace of the bromethylated monophosphonium had been formed : its

absence was carefully proved by a special experiment. The bromides were then transformed into chlorides and the latter precipitated by dichloride of platinum; the mother-liquor filtered off from the copious precipitate of the diphosphonium-salt was considerably evaporated, when, on cooling, well-formed octohedra were deposited, which on analysis were found to contain



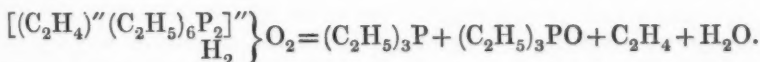
The formation of the vinyl-compound under these circumstances is easily explained:



The amount of vinyl-compound produced is but very small in proportion to that of the other salts which are formed in the mutual action between triethylphosphine and dibromide of ethylene.

ACTION OF HEAT UPON THE HYDRATE OF THE DIPHOSPHONIUM.

The hydrate, when submitted to the action of heat, undergoes a series of remarkable changes, which I have studied with lively interest. The decomposition commences at 160° ; on raising the temperature gradually to 250° , the whole of the hydrate passes over in the form of liquid and gaseous products. The liquid product consists of triethylphosphine and oxide of triethylphosphine; the gas contains a considerable proportion of ethylene, which is readily characterized by its deportment with bromine. This transformation may be represented by the following equation:

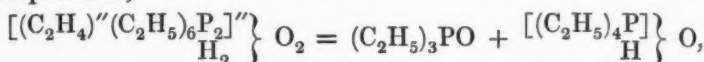


The study of the changes, however, through which the hydrate runs before it is broken up, shows unmistakeably that this equation can represent but one phase, even of the final transformation of the diphosphonium-compound. The study of the intermediate changes presents unusual difficulties, and I confess at once that I have failed to solve the problem to my entire satisfaction.

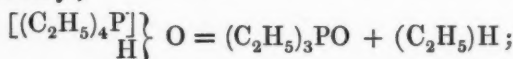
The experiments carried out with the view of disentangling the intricacies of these reactions, will perhaps be better understood if I commence by setting forth the ideas which I have ultimately formed of these metamorphoses, and then describe the experiments on which they are founded.

Under the influence of heat, the hydrate of the diphosphonium undergoes two principal transformations, which are accomplished

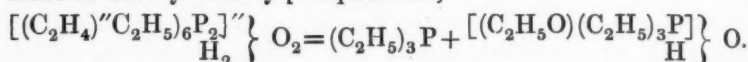
side by side. A portion of this compound gives rise to the formation of oxide of triethylphosphine and hydrate of tetrethylphosphonium,



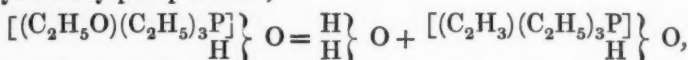
the latter splitting ultimately into oxide of triethylphosphine and hydride of ethyl,



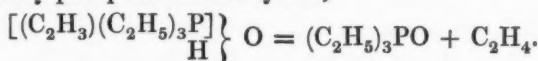
while a second portion is resolved into triethylphosphine and hydrate of oxethyl-triethylphosphonium,



The latter may undergo, at a high temperature, a further transformation, separating, partially at least, into water and hydrate of vinyl-triethylphosphonium,



the vinyl-compound yielding, in the last stage of the reaction, oxide of triethylphosphine and ethylene,



The separation of triethylphosphine and its oxide by the action of heat upon the hydrated diphosphonium requires no special experimental demonstration. To individualize the other compounds, the following experiments were made:—A considerable quantity of the dihydrate was evaporated in a retort in an atmosphere of hydrogen. As soon as the phosphorus-base began to distil freely—at about 190°—the operation was interrupted, and the residuary alkaline liquid saturated with hydrochloric acid and precipitated with dichloride of platinum. A dingy yellow amorphous precipitate was thrown down, insoluble in cold water; and the mother-liquor, on evaporation, furnished a mass of deep orange-red octohedra, which were transformed into the corresponding iodine-compound. The salt thus obtained proved unmistakeably a mixture of two compounds of different solubility. The less soluble was obtained in beautiful crystals, exhibiting all the characters of iodide of tetrethylphosphonium. The formation of a tetrethylphosphonium compound, in this reaction, was identified by the analysis of the iodide, the platinum-salt and the gold-salt.

The result of analysis was most satisfactorily confirmed by the crystallographical examination of the salts under consideration. Q. Sella has compared the crystals of the iodide above men-

tioned with crystals of iodide of tetrethylphosphonium obtained in the usual way. I have appended at the conclusion of this paper the elaborate investigation of this beautiful salt, with which my friend has furnished me.

Far less conclusive is the experimental evidence which I was enabled to collect in support of the opinion, that the hydrate of tetrethylphosphonium formed by the action of heat on the hydrated diphosphonium is accompanied by the oxethylated triethylphosphonium compound. The principal argument in favour of this view is the abundant evolution of triethylphosphine, which cannot be understood unless we assume the simultaneous formation of the oxethylated, or of the vinyl-compound. I have failed in my endeavours to prepare the more soluble iodide which accompanies the tetrethylphosphonium-compound in a state of purity. Nor was the attempt to separate the two compounds in the form of platinum-salts rewarded by better success. Both platinum-salts crystallize in octohedra which differ but slightly in solubility.

The experimental numbers obtained in the analysis of these octohedra characterize a mechanical mixture of the two platinum-salts.

The action of heat upon the hydrate of the diphosphonium induces yet another transformation, to which I have already alluded when mentioning the dingy yellow insoluble precipitate which is formed on addition of dichloride of platinum to the product of the action of heat upon the hydrate, neutralized with hydrochloric acid.

The following paragraph contains the fragmentary information which I have collected in studying these changes.

PARADIPHOSPHONIUM-COMPOUNDS.

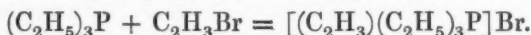
The basic compound which yields the amorphous yellow platinum-salt repeatedly mentioned, is a transient product of the action of heat on the hydrated diphosphonium. If during distillation, the alkaline residue in the retort be tested from time to time with dichloride of platinum, a point is soon reached, when instead of the slightly crystalline precipitate, perfectly insoluble in dilute hydrochloric acid, which appears at the commencement of the operation, an amorphous, generally dingy yellow precipitate is obtained, immediately dissolving on addition of a few drops of dilute hydrochloric acid. If the distillation be now interrupted, and the residue neutralized with hydrochloric acid, and mixed with a few drops of dichloride of platinum, a discoloured precipitate is thrown down, the filtrate from which, on addition of a further quantity of platinum-solution, yields the amorphous salt, of a light yellow colour, and in a state, of purity. This salt exhibits no

trace of crystalline structure, even when examined under the most powerful microscope: in the perfectly dry state, it is remarkably electrical, flying about in all directions during trituration.

The same substance is obtained when the hydrated oxethyl-triethylphosphonium is submitted to the action of heat. By interrupting the process at a convenient time, and adding dichloride of platinum to the neutralized residue, phenomena identical with those just mentioned are observed.

The compound which produces the amorphous yellow precipitate was lastly obtained, under the following circumstances.

While I was engaged with the study of the vinyl-compounds, the examination of which is described in one of the previous paragraphs of this paper, the idea suggested itself that the bromide of vinyl-triethylphosphonium might also be formed by the action of bromide of vinyl ($\text{C}_2\text{H}_3\text{Br}$) on triethylphosphine:



In performing the experiment, I had an opportunity of observing the sluggishness of action of this bromide, often previously noticed in experimenting in the ammonium-series. When gaseous bromide of vinyl is passed through triethylphosphine, not a trace of it is fixed by the phosphorus-base. Triethylphosphine may be distilled in an atmosphere of the bromine-compound without undergoing any alteration. Bromide of vinyl, freed from every trace of adhering dibromide of ethylene by repeated distillation at a low temperature, and subsequent washing with lukewarm water, was therefore enclosed, together with triethylphosphine, in a strong glass tube. No change was perceptible after two days' digestion at 100° ; and it was only on the third day that a thin layer of viscid matter began to separate at the bottom of the tube. The digestion was then continued at a higher temperature; and after the mixture had been exposed for three days longer to a temperature varying from 160° to 180° , about half the fluid was found to be converted into a solid mass, while a limpid liquid floated on the top. On opening the tube, cooling it well at the time, the liquid effervesced strongly, and a gas escaped which burned with a green-edged flame, and appeared to consist, partly at all events, of the vapour of unaltered bromide of vinyl. In subsequent repetitions of the experiment, it frequently happened that the tubes were shattered by the sudden expansion of the compressed gas: hence probably permanent gases are formed in the reaction. The liquid decanted from the solid proved to be a mixture of undecomposed bromide of vinyl with free phosphorus-base; the solid mass was found to consist of several bodies. On dissolving it in water, a rather small quantity of a sparingly soluble, beautifully crystalline, nacreous salt separated out, the composition of which is at present undetermined. By treatment of the filtered solution with oxide

of silver, a strongly alkaline liquid was produced, which, when neutralized with hydrochloric acid and precipitated with dichloride of platinum, gave at once the amorphous yellow platinum-salt easily soluble in dilute hydrochloric acid.

On analysis, this salt furnished results which characterize the platinum-compound of ethylene-hexethyl-diphosphonium.

Nevertheless the two substances are not identical. In addition to the difference in the physical properties and in the behaviour with dilute hydrochloric acid, the two salts exhibit other well-defined marks of distinction. The crystalline salt is perfectly insoluble in water, even when boiling. The amorphous salt dissolves readily, and is deposited again on cooling in the same amorphous condition. In designating this peculiar molecular variety as paradiphosphonium-compound, I simply wish to distinguish it from the salt of the ordinary diphosphonium, without giving any opinion respecting the nature of the difference. The existence of the diphosphonium-compounds in the crystalline and in the amorphous condition, reminds us of the behaviour of some of the native organic bases under the influence of heat. It is well known that several of these substances, which are remarkable for their powers of crystallization, are rendered perfectly amorphous when heated for some time above their melting-point.

As might have been expected, the paradiphosphonium-compounds are slowly and gradually reconverted into the ordinary diphosphonium-salts.*

The hydrated paradiphosphonium, when separated from the platinum-compound by successive treatment with sulphuretted hydrogen and oxide of silver, yields with hydriodic acid a gummy mass which only gradually assumes the crystalline form. By a considerable number of recrystallizations, the characteristic diiodide was ultimately obtained with all its properties; when converted, by treatment with chloride of silver, into the dichloride, and precipitated by dichloride of platinum, it immediately yielded the well known crystalline precipitate so frequently mentioned in this paper. Both salts, the iodide and the platinum salt, were identified by analysis.

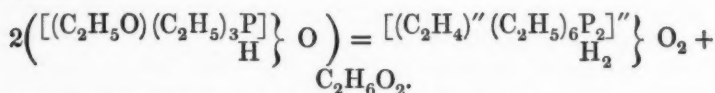
The transition of a diphosphonium-compound from the crystalline to the amorphous, and from the amorphous to the crystalline condition, appears intelligible enough†. The transformation of the oxethylated monophosphonium, however, into a diphosphonium-compound, and the formation of the latter by the action of

* In several experiments, the reaction between bromide of vinyl and triethylphosphine gave rise to the formation of a mixture of the amorphous and crystalline diphosphonium-compounds.

† The diphosphonium-salt, which is formed by the action of sulphocyanate of ethylene upon triethylphosphine (Chem. Soc. Qu. J., vol. xiii. p. 320,) in the first place, likewise yields the amorphous platinum-salt when precipitated by dichloride of platinum.

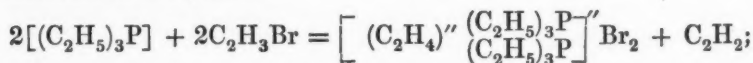
bromide of vinyl upon triethylphosphine, claims our attention for a moment.

The conversion of the hydrate of oxethyl-triethylphosphonium* into the hydrated diphosphonium is readily understood, if we remember that two molecules of the former contain the elements of one molecule of the latter and of one molecule of ethylene-alcohol:



I am unable to say whether the group $\text{C}_2\text{H}_6\text{O}_2$ actually separates as ethylene-alcohol, or, which is more probable, in the form of water and oxide of ethylene, or even of aldehyde. Material and patience began to fail when I had reached this point, and I must reserve the decision of this question to later experiments†.

The same remark applies to the final elucidation of the reaction between triethylphosphine and bromide of vinyl, which, as I have pointed out, likewise gives rise to the formation of diphosphonium-compounds. Two molecules of triethylphosphine and two molecules of bromide of vinyl contain the elements of one molecule of dibromide of the ethylene-diphosphonium and one molecule of acetylene:

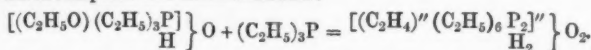


and experiment proves that a considerable amount of permanent gas is generated in this reaction; but there are other products formed, and it would be idle to dwell any longer on the interpretation of these unfinished observations.

In conclusion, I append Q. Sella's crystallographical examination of the iodide of tetrethylphosphonium, to which I have

* I need scarcely mention that the purity of the compound used in my experiments had been established by a special analysis. When prepared from imperfectly purified bromethylated bromide, the oxethylated base is apt to contain minute quantities of the hydrate of the diphosphonium.

† The convertibility of the oxethylated triethylphosphonium-salts into diatomic compounds has induced me to try whether the action of triethylphosphine upon them would accomplish this transformation:



But even when heated up to 150° , the two bodies remain unaltered; nor is there any action when the oxide is replaced by the bromide of oxethyl-triethylphosphonium.

alluded in the latter portion of this paper, and also the results obtained by him in measuring the corresponding platinum-salt.

Crystalline form of Iodide of Tetrethylphosphonium.

“System rhombohedric :—

$$111,100 = 59^{\circ} 32'.$$

Forms observed:—

111, $10\bar{1}$, 100, 110, 210, $31\bar{1}$
(Fig 47).

Forms observed:—

$$a', d', P, b', b^2, e_3.$$

Fig. 47.

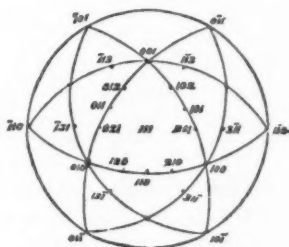


Fig. 48.

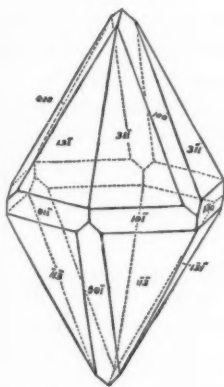


Fig. 49.

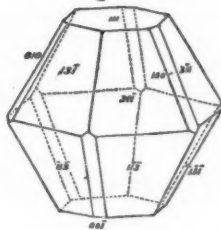
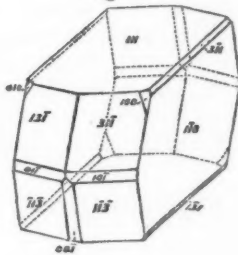


Fig. 50.



Combinations observed :—

$31\bar{1}; 100, 10\bar{1}$ (Fig. 48).

$31\bar{1}, 111, 100$ (Fig. 49).

$31\bar{1}, 111, 10\bar{1}; 100$ (Fig. 50).

$31\bar{1}$, 110 , 100 ; $10\bar{1}$, 210 (Figs. 51 and 52).

$31\bar{1}, 100, 110; 10\bar{1}, 210, 111.$

The crystals prepared by treating triethylphosphine with iodide of ethyl exhibit the forms Figs. 51 and 52.

Fig. 51.

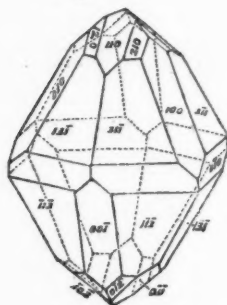
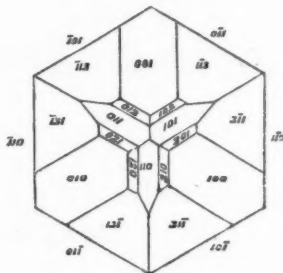


Fig. 52.



The crystals obtained by submitting the hydrated diphosphonium to the action of heat and neutralizing the alkaline residuary product with hydriodic acid, have the form Fig. 48, when rather large and slightly yellow, and the forms Figs. 49 and 50, when minute and perfectly white.

The crystals of the form Fig. 50 are most frequent; they seem to have adhered to the vessel with one of the larger faces of the prism $10\bar{1}$.

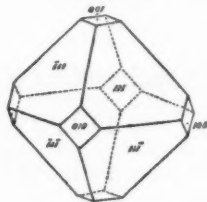
Crystals distinct. Lustre on the faces, except 111 , very great.

Crystals optically positive. The indices of refraction are for the ordinary ray $\omega = 1.660$, for the extraordinary ray $\epsilon = 1.668$.

The crystals of iodide of tetrethylphosphonium are isomorphous with those of iodide of silver. In the latter substance, $111, 100 = 58^\circ 27'$, instead of $59^\circ 32'$, found in the tetrethylphosphonium-salt. Both salts have the same hexagonal habitus, and both are optically positive."

Crystalline form of the Platinum Salt of Tetrethylphosphonium.

Fig. 53.



"System monometric:—

Forms observed:—

$100, 111$ (Fig. 53).

The faces of the cube 100 are very brilliant; those of the octohedron 111 are often hollow.

No influence on polarized light.

Colour orange-red."

IX.—*On the Ice found under the surface of the Water in Rivers,
called Ground Ice.*

By RICHARD ADIE. Liverpool.

THE ice found in the bed of a river or running stream under the surface of the water, is a subject which has engaged the attention of men of science, to endeavour to account for its occurrence in an apparently unnatural position, while it has also forced itself on the attention of practical men, on account of the mischief which an accidental obstruction, such as a branch of a tree lodged in the bed of a mill-course has been found to occasion when the water is charged with ice particles.

I believe that I was among the first to state that ground-ice is formed in the coldest part of a stream, and that the small crystals, immediately after they are formed, are carried along by the current, submerged and entangled by plants or other obstructions in the bed of the stream suitable for their detention.

In the recent frost of December and January 1860–61, I searched for ground-ice where, in past years, I had found it. Yet, though this frost was the most severe that has visited us during the sixty years of the century, I found ground-ice only in one locality,—a shaded place, where I was induced to search for it from seeing bundles of ice-crystals floating down the stream; for I had before observed that where ground-ice exists, some of it is constantly breaking off from the moorings. In this instance, the ice surrounded a stone covered over by the water of a rivulet which leaves the Marquis of Abercorn's grounds at Duddingston, near Edinburgh.

The other streams which I examined in the neighbourhood of Edinburgh shewed no floating crystals or other indications of the presence of ground-ice; they appeared to be well supplied with water, which, coming from underneath a covering of snow, was unfavourable for showing this kind of ice.

In the frosts of 1854 and of 1855, I found ground-ice in a number of rivers. These frosts differed from the recent one by penetrating into the ground to a greater extent. In 1854, the

frost entered into the ground to the depth of $11\frac{1}{2}$ inches, and that of 1855 to $13\frac{1}{2}$ inches. In 1860-1 the earth had merely a crust of frozen soil under the snow.* The general calmness of the weather must likewise have had influence; for, in an exposed district in the neighbourhood of Liverpool, I have repeatedly found quantities of ground-ice after two days' moderate frost, accompanied by a dry brisk wind.

Those who have examined ground-ice appear to think that the water has frozen in the bed of the river, the current preventing it from freezing in its natural place—the surface. The appearance of the masses formed do not favour this view: for many shady positions in streams are noted for exhibiting collections of ice that could never have frozen there. To ascertain the nature of ice, when formed under water, on the sides of a containing vessel, I produced it rapidly by a freezing mixture, when the ice assumed a very hard form.

A small stream about twelve miles from Liverpool, where it joins the river Alt, is extremely favourable for showing the phenomena of ground-ice in an open exposed district. I first saw it there in December, 1846; and as I have since often examined the ice in the beds of streams, I wish to mention that the circumstance which appears to me most favourable for its formation, is wind accompanying the frost. On 13th December, 1846, the ground-ice was plentiful; my note at the time states that the frost had not been severe, but the air had been very dry, with a brisk wind.

Ground-ice is capricious both in its time and place of settlement. On 3rd January, 1854, I saw it in very large quantities in the bed of the Eden a little above Carlisle. In February, 1855, after a frost which had gone deeper down in the ground than the one of the previous year, I searched the same part of the Eden without seeing any; there were a sufficient number of loose ice crystals floating down the stream to render it probable that ground-ice existed higher up. On the same day I had seen ground-ice in the Ribble above Preston, but none in the Lune above Lancaster.

After I had become satisfied that the position of ground-ice is

* Since the above was written, the writer has been informed by a friend residing fifteen miles west of Edinburgh, where the snow was not so deep, that the frost in that locality penetrated the ground to the depth of an inch; and in a very few places, where the ground had been denuded of snow by the wind, the earth was frozen to the depth of thirteen inches.

one of lodgment merely, I have been in the habit of searching for it where the streams pass under stone arches and places most unfavourable to freezing, and in these localities I have several times found it. The masses I have referred to, as seen in the Eden in 1854, must have been lodged there: for they contained throughout their substance a few water-worn pebbles, and they were all inclined towards the current from whence they were receiving continual supplies. I could not get at the collections of ice to measure them, as they were all under the surface in a deep-flowing part of the stream; but one rose so near the surface as to give a ripple to the current, and appeared to be from 4 to 6 feet high.

Note on Mr. Adie's Paper "On Ground Ice."

By E. FRANKLAND, F. R. S.

THE formation of ground-ice has excited considerable interest amongst the observers of natural phenomena, and various suggestions have been made to account for its production. One of the most ingenious of these assumes that, in rapidly-flowing streams, the eddies and currents cause such a constant intermingling of the upper and lower water-strata, as to render the whole mass of the stream of one uniform temperature. When such a stream becomes cooled down to the freezing-point, the usual surface-layer of cold water below 39.5° F. cannot of course be formed. The rocks and other solid bodies in the bed of the stream continue, however, to radiate heat through the water into the atmosphere, and thus become reduced in temperature below the freezing point; the necessary consequence of such a state of things being the formation and gradual accumulation of ice around such solid bodies.

The latter part of this hypothesis appears to be untenable, inasmuch as water is absolutely intranscalent to rays of *obscure* heat: consequently, the passage of such rays from the bed of the stream through a stratum of water is absolutely impossible. It appears to me that the formation of ground-ice, which is well known to take place only in rapidly-flowing streams, depends upon the fact that ice, like other crystalline bodies, deposits itself more readily upon rough surfaces,—freezes, in fact, at a somewhat higher temperature when in contact with such surfaces, than within the mass

of liquid itself. Hence, when a rippling stream is cooled to the freezing point, ice-crystals attach themselves to the pebbles and other objects in the bed of the river, these crystals forming equally inviting nuclei for the further deposition of larger quantities of ground-ice.

The tendency of ground-ice to form in shady places, as mentioned by Mr. Adie, is an interesting observation, which may probably find an explanation in the circumstance that water and ice, although perfectly unable to transmit obscure rays of heat, are yet to a certain extent transcendent to luminous heat. Tyndall has shown that certain interior portions of a block of ice may be melted by luminous heat, which has already passed through a considerable thickness of ice; and it is well known that if a mass of ice containing an embedded pebble be exposed to the solar rays, the ice around the pebble soon becomes melted. Any exposure, therefore, of ground-ice and its supernatant water to solar radiation would have the effect of warming the non-icy nuclei; thus remelting during the day, a portion, at least, of the ground-ice which had been formed during the previous night: consequently such an exposure must be regarded as presenting an obstacle to the formation of this kind of ice, although it is well known to favour the production of the ordinary surface ice.

X.—*On the Putrefaction of Bile, and the Analysis and Theory of Gallstones.*

By DR. THUDICHUM.

In October, 1859, I communicated to the Medical Society of London a Paper, in which I described casts of the biliary ducts, which I had discovered in the centre of human gallstones. As these casts consisted principally of brown colouring matter of bile, or that modification of cholechrome termed *cholophaeine*, I first studied the chemical nature of that substance, in order the better to understand its bearing on the processes in which it played so conspicuous a part. The results of these inquiries I communicated to the Physiological Section of the British Association for the Advancement of Science, at the Oxford Meeting in 1860, and an

abstract of my communication has appeared in the "British Medical Journal" for July 14th, 1860. I proved that cholochrome is an amido-acid; that it is decomposed by nitrous acid, with evolution of nitrogen, and yields a new acid---*cholochromic acid*,---which is free from nitrogen, and in its crystallized state resembles the substance termed by Virchow "*hæmatoïdine*," but, nevertheless, differs from it in many particular properties. I described several other products of decomposition and reactions of cholochrome, and, among them, the most important one, viz., that it is precipitated during the putrefaction of bile from the solution in which it was held by the healthy fluid. This led to the re-investigation of the process of putrefaction of bile, which had already been instituted by former observers; and I was not merely enabled to confirm the principal features of the description given by Gorup-Besanez, but also to add some new facts, explain the origin of some substances discovered by him, and construct a theory of this process of decomposition, which led me up, almost in a straight line, to the theory of gallstones. On subjecting large quantities of material to chemical analysis, these concretions yielded the same substances as those which made up the deposit of putrid bile, with the sole exception of mucus, of which little or none could be found in gallstones. Of these researches I gave a short account to the British Medical Association at their Annual Meeting, held in 1860, at Torquay. While able to accompany the leading ideas by the exhibition of specimens, progressively proving every step of my analyses, the limitation of the time imposed upon me by circumstances on that occasion did not permit me to do justice to the subject. I therefore more fully expounded my ideas before the Medical Society of London, in a Paper read before them on October 8th, 1860, and reported, in abstract, in the "British Medical Journal" for October 13th, and the contemporaneous numbers of the other medical periodicals. I then exhibited cholochrome, cholic acid, and earthy salts, as essential constituents of gallstones in man and animals. I characterized the cholesterine in gallstones of man as a secondary ingredient, calling for new analyses to prove the freedom from cholic acid of concretions reported to have consisted of pure cholesterine. Having come to the conviction that the binding material of gallstones is cholic and choloidic acid, I eliminated as untenable, the idea of an inspissation of mucus in the formation of these concretions, which had hitherto been the groundwork of all speculations upon their origin.

In the present communication I propose to give a short analysis of my results as a preliminary guide to the reader, and then to describe the chemical proceedings which I adopted for the purpose of ascertaining the composition of human and bovine gallstones and of ox-bile.

Theory of Gallstones.

In some examinations of human gallstones, I had found a resinous biliary matter; but, owing to the small quantity and the refractory nature of the substance, and particularly to the difficulty of separating it, I had not been able to identify it. The examination of some ox-gallstones afforded an opportunity for settling this point. I extracted a large quantity of cholic and choloidic acid from them,—a quantity such as could never be derived from any bile with which the calculi might be supposed to have been soaked at the time they were taken out of the gall-bladder. There could be no doubt that both cholic and choloidic acids had been deposited, together with the cholochrome, during the pathic process in the living animal.

The presence in almost all biliary concretions of some earthy and alkaline salts, points in the same direction. They are, and were, in my analyses, either present as phosphates and carbonates of lime and magnesia, and could be extracted by hydrochloric acid, or they were combined with the colouring matter of bile, and with stearic and palmitic acid. In gallstones from man, the colouring matter was accompanied by a larger proportion of inorganic salts; but in gallstones of the ox, the quantity of cholochrome preponderated to so extraordinary a degree over the earthy matter, that it must be assumed to be present in the free state, and not, as Bramson supposed it to be, always, viz., combined with lime.

Cholochrome, cholic, and choloidic acids, and earthy salts, thus present themselves as substances without the concurrence of which the more common forms of gallstones would rarely be formed; they are, in other words, essential ingredients of gallstones. In man, gallstones contain a large amount of cholesterine in most cases, but that is a secondary ingredient, as the phosphatic crust is of the uric acid, or oxalate of lime calculus from the urinary bladder, and is mostly crystallized around the other matters forming the nucleus. There are human gallstones, which, like those from the ox, contain no cholesterine. Others are said to consist entirely of chole-

sterine,—a statement which has to be verified by fresh analyses, which must prove the absence of cholic and choloidic acid. In gallstones from man, stearate and palmitate of lime are mostly present; and it remains to be seen how far those substances can assist in effecting the concretion of the detached particles of cholechrome, which I now ascribe to the cholic and choloidic acid. Let us therefore dismiss the hypothesis of the inspissated mucus, or the inspissated bile, which figure in our pathogeny as the mortar which combines the particles of the nucleus: mucus is not found in gallstones; and an inspissation in the midst of fluid bile is quite incomprehensible. Moreover, even an indubitable inspissation of bile could not lead to an insoluble concretion. We may, therefore, reject this hypothesis, and admit that *the binding material of the nucleus of gallstones is cholic acid, or choloidic acid, or both.*

The process by which gallstones are formed appears analogous to that which produces that rare description of calculus in the urinary passages,—the phosphatic or fusible calculus. It is a decomposition of the bile akin to putrefaction. The compound amido-acids split up into their constituents, under the influence of a cause which remains to be ascertained, but is probably a putrid ferment absorbed from the intestinal canal. Under the influence of a little acetic acid, formed out of glycocoll, and some other new acid produced by the putrefactive change, perhaps valerianic acid, cholechrome, a quantity of cholic acid, and a portion of choloidic acid, together with some salts and little fat, are deposited. This is the process in the ox, and sometimes in man. But the bile of man differs in this respect from that of the ox, that it contains cholesterine, while that of the ox contains, at the most, only a very small quantity as compared to the other. This cholesterine is dissolved in the taurocholate of soda. But as soon as the acid of this salt is decomposed, the cholesterine is set free, crystallizes, and deposits upon any particle that may happen to be within easy distance, in the manner of all crystals, which like to post themselves upon prominent bodies.

Numerous are the modifications which this process may undergo; but their discussion must be reserved for future occasions. The presence of chloride of sodium, iron, copper, and other inorganic matters in gallstones, has no doubt a significance in each case, but a subordinate one. In some gallstones from the ox, I have again found a sulphurous compound, already observed by Bolle in 1852. When boiled with hydrochloric acid, they gave out vapours which

smelt like sulphuretted hydrogen, and blackened lead-paper. I collected them in caustic potassa, mixed with some solution of arsenious acid. On subsequent acidification, a yellow, somewhat orange-coloured deposit of a sulphur-compound of arsenic was formed; but after drying, it had become brown and hard, and on sublimation, yielded tersulphide of arsenic, besides leaving a quantity of charcoal; thus proving that the gas was a compound of a carbonaceous and a sulphurous body in a volatile form, or a mixture of two analogous substances.

Putrefaction of Bile.

Some large bottles, full of bile, and well stoppered, had been allowed to stand for the period of two years and one year respectively. The bile had assumed a feebly acid reaction, a bright port wine colour, and had deposited a copious flaky, green and brown deposit, mixed with white chalk-like particles and greenish crystals. This deposit, on analysis, was found to consist of cholochrome, cholic acid, phosphate of lime and magnesia in dichroic crystals, and mucus. The fluid part of the bile was found to contain principally choloidate of soda, with little cholate, taurine, valerianate, and acetate of soda and ammonia, phosphate of soda, but no glyco-coll, nor any glycocholic or taurocholic acid. It was quite clear that the bile had spontaneously undergone a decomposition similar to that which is effected by boiling with acids or alkalies,—a decomposition which, in its main features, has already been described by Gorup-Besanez. Glychocolic and taurocholic acids had split respectively into glycocoll, taurine, and cholic acid. The cholate, probably, or some other decomposing substance, had yielded valerianic acid, which had combined with soda, or with ammonia, which latter probably originated in the decomposition of glycocoll. This compound being the amido-acid of acetic acid, no doubt in this process, as in the putrefaction of urine, yielded the acetic acid, which combined with the necessary amount of soda, and precipitated a portion of the cholic acid, while the greater portion of this acid remained in solution combined with soda, and became further metamorphosed into choloidic acid, and perhaps other products of decomposition of an acid nature. The cholochrome had no doubt been precipitated by the new acid before cholic acid, as its acid properties are much less pronounced.

The port wine colour of the fluid was probably due to some metamorphosed cholochrome, possibly cholochromic acid, or a derivate. That cholochrome, cholic acid, and crystallized phosphates are precipitated in this process had not been observed by Gorup-Besanez, who had also neither found valerianic acid, nor explained the origin of the acetic acid, which he undoubtedly discovered.* These observations, then, and the theory of the process, are my own additions to the doctrine.

Gorup-Besanez extracted also a mixture of fatty acids from putrid bile, among which he believed to have recognized margaric acid. This acid, or its fellow, stearic acid, is a component of the first deposit formed in putrid bile. But, like cholesterine in ox-bile, this ingredient is too easily lost sight of, in consequence of the small quantity in which it is present.

When Gorup-Besanez allowed bile to decompose at a temperature of from 25° to 30° R, exposed to the free access of the air, for a period of three weeks, he obtained choloidic acid as the principal product of decomposition. When, however, he exposed bile to the air for three months, in a cellar, at a temperature varying between 10° and 12° R, he found cholic acid instead of choloidic. In both cases, the decomposed mass had an offensive ammoniacal smell and a marked alkaline reaction. Taking into consideration only one element, viz., that of time, he concluded that choloidic acid was the forerunner of cholic acid; that the latter was produced from the former; that the presence of cholic acid was evidence of a more advanced stage of decomposition than that of choloidic acid. But he omitted to take into consideration the most important fact, —that the specimen of bile which yielded the cholic acid had been subjected to a much lower temperature than the specimens which yielded the choloidic acid, and had thus been influenced by circumstances which, above all others, retard the decomposition of animal matters. His assumption, therefore, while unsupported by any direct proof, is opposed by the fact, that we know choloidic acid only as a product of decomposition of cholic acid; that we cannot reproduce cholic from choloidic acid; and further, by the results of my own investigations, which showed that bile, after one year's, and after two years' decomposition, contained principally choloidic acid; a portion of this biliary element only being precipitated in the form of cholic acid. This precipitate, it is but right

* Ann. Ch. Pharm. lix, 129.

to conclude, was produced at a time when cholic acid prevailed: for had choloidic acid prevailed at the time of the formation of the new acid (acetic, valerianic, and others), the deposit must have consisted of choloidic acid, or at least contained some choloidic acid, while in fact it contained hardly any, or none. No cholic acid remained in solution. On account of these facts, I believe that we must reverse the order of succession assigned to those acids by Gorup-Besanez, giving to cholic acid priority in time, to choloidic acid ultimate supremacy, and ascribing to its break-up into the fatty acids above-mentioned the destruction of the biliary state.

Bile decomposed at a moderate temperature during nine months, was found by Gorup-Besanez to exhibit an acid reaction, due to the presence of acetic acid in a free state. It consequently had the same reaction as the specimens examined by myself. He does not state in what condition the biliary acid was present; which is much to be regretted, as free acetic acid could not be present so long as any cholate or choloidate remained in solution, the acids of which salts, in his analyses, he always precipitated by acetic acid.

Diagram exhibiting the Decomposition of Bile.

First Stage. The bile is neutral or alkaline.

Taurocholate of soda	yields	{ Cholate of soda. Taurine.
Glycocholate of soda	yields	{ Cholate of soda. Glycocoll.
Margarate (Palmitate) and stearate of lime		} are deposited.
Phosphate of lime and magnesia		

Second Stage. The bile becomes acid by the supervention of a new (valerianic?) acid, whose origin is undecided.

Cholate of soda deposits cholic acid.

Soda-salt of new acid is formed.

Cholochrome (Cholophaeic acid) is precipitated, and partly transformed into soluble cholochromate (?)

Glycocoll	yields	{ Acetic acid. Ammonia.
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Third Stage. The bile continues acid.

Cholate of soda is transformed into choloidate. The latter deposits some choloidic acid (?).

Choloidate of soda yields fatty acids, products of decomposition; among them, probably derived from glycocoll, acetic acid, in the free (?) state.

The alkaline condition during the first stage, observed by Gorup-Besanez, occurs only when bile putrefies at a high temperature, so that the mucus undergoes active decomposition, and produces ammoniacal compounds. The bile upon which I operated, at low temperatures, and with moderate access of air, I could not at any time discover to be alkaline. In one case, Gorup-Besanez observed the acid reaction to give way to a second alkaline reaction, but did not notice any corresponding essential changes. Owing to these uncertainties, I have not distinguished as stages the neutral, alkaline, acid, and last alkaline conditions. Gorup-Besanez is of opinion that the decomposition of the primary biliary acids is not effected until an acid reaction of the bile appears; because only at that juncture does acetic acid produce a precipitate of cholic or choloidic acid. But this negative test appears to me only relative: because the acids may be decomposed, and yet acetic acid may produce no immediate precipitate, more acetic acid being required to cause a precipitate at the period when the bile is yet neutral or alkaline, and when no adventitious acid has yet taken the edge off the alkaline phosphate of soda, which is invariably present in bile, and though not very evident to test-paper, neutralises some acid before an acid reaction can become established. To the naked eye, the first stage is characterized by the deposition of white granules, partly on the top of the fluid, partly at the bottom, partly against the walls of the vessel, which consist of palmitate, stearate, and phosphate of lime. All the stages no doubt gradually pass into each other; and the above diagram, while considered useful for illustration, must not be considered as an absolute syllabus of a variable process.

Analysis of human gallstones.

I must here distinguish between the general analysis of gallstones, by which the essential constituents are found, and those special processes which are directed to the isolation of certain less

frequent ingredients, such as copper, manganese, sulphides, or uric acid. Those human gallstones which consist principally of cholochrome, are to be analysed by the process which will be detailed lower down as applicable to gallstones from cattle. For the analysis of the common cholesterine concretion from man, the following process will be found suitable.

The powder of the calculi is gradually thrown into hot benzole, contained in a flask, placed on a sand-bath. The cholesterine and biliary matters are dissolved, while cholochrome, earthy phosphates, earthy salts of fatty acids, and any other ingredients remain suspended and unchanged. Solution and residue are separated by filtration. The matter on the filter is washed with repeated quantities of benzole, lastly with cold alcohol, and dried. It then presents itself as a brown powder, which is very delicate to the touch, imparting an almost velvety feel. Treated on the filter with absolute ether containing little nitric acid, it yields fatty acids to the ether, which, on distillation of the ether from the filtrate, are deposited in a granular and crystalline form. If the residue on the filter is next treated with water, phosphate and nitrate of lime and magnesia are extracted, and remain as phosphates and carbonates, sometimes coloured blue by copper, on evaporation of the solution and incineration of the residue. The colouring matter, extracted with ether and nitric acid and water, is free from fatty matter, but retains some earths, which can only be obtained by burning the cholochrome, or by dissolving it in carbonate of alkali, when the earthy and other insoluble inorganic and organic matters remain behind. They are then incinerated and the ashes added to the earths extracted by acid and water.

The carbonate of lime may be recognized by the effervescence, which takes place on dissolving the earthy salts in hydrochloric acid. The subsequent addition of ammonia in excess precipitates the phosphates, while the lime which before had been as carbonate, remains in solution, and may be precipitated by phosphate of soda or oxalate of ammonia. From the original benzole solution, cholesterine is best obtained by evaporating the solvent, and treating the residue with boiling spirit of wine. On cooling, the cholesterine, which before had been greenish, crystallises in the usual glistening white plates, while the solution retains the brownish-green coloured biliary matters. On evaporation, a small quantity of a mixture of cholesterine and fat is deposited. That

and the rest of the alcohol being removed, there remains a brown resinous mass, insoluble in water, soluble in alcohol, and soluble in caustic potassa; an excess of caustic ley added to the solution causes the separation of a resinous salt, which floats on the top of the caustic fluid. From the solution in potassa, it is precipitated by hydrochloric acid. It combines with lime and baryta, forming insoluble compounds, and is therefore choloidic acid, though brown and impure, and perhaps, as suggested by the analysis of ox-gallstones, mixed with some cholic acid. It yields a small quantity of matter to boiling water; but the nature of this extract could not be determined by crystallization, as was the case in the analogous extract from ox-gallstones.

In his directions for analysing human gallstones, Simon refers hypothetically to the presence of biliary resin, without, however, stating its presence as a positive occurrence, or grasping its significance. In the ordinary analysis of gallstones, which began with the extraction of the powder by means of caustic potassa,—a process mainly directed to the purification of cholesterine, choloidic (and cholic) acid remained with the cholochloine produced, from which it could afterwards be scarcely separated. When the analysis of gallstones had, however, for its principal object the preparation of cholophaeine, the spirituous mother-liquor of cholesterine was not thought of sufficient importance to deserve further scrutiny; and even if it had been granted, it is possible that the fatty salts dissolved by the boiling spirit (which, in the analysis with benzole, remain undissolved, and are subsequently decomposed with acid and extracted with ether and water), would have made the separation of the choloidic acid a matter of considerable difficulty.

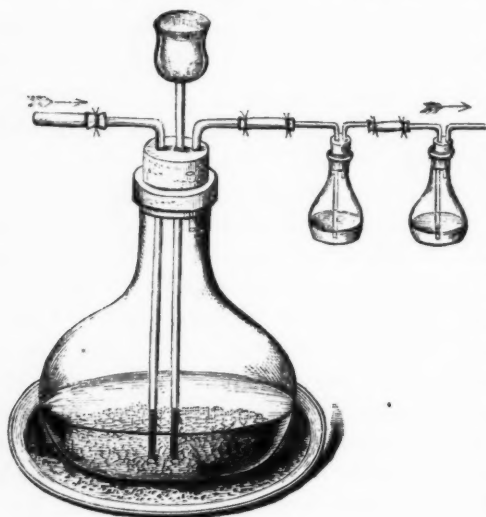
Analysis of ox-gallstones.

The gallstones are powdered, and boiled with water during three hours. The dark-brown extract is removed by filtration, and the residue on the filter washed during three days with boiling water,—that is, until the filtrate comes away colourless. The powder is then dried in the water-bath. The water-extract is evaporated.

It is then boiled for several hours with alcohol of 80° strength, which also acquires a dark colour, and is separated by filtration. The residue is for several days washed with boiling alcohol, and dried. The primary filtrate is allowed to cool by itself and the

washings are evaporated by themselves. The alcoholic extract is further analysed, as will be detailed lower down.

The powder is next mixed with water in a flask, and a quantity of hydrochloric acid added. A slight frothing ensues, and the smell of sulphuretted hydrogen is at once perceptible; lead-paper is turned black by the gas. It is therefore necessary to perform the extraction with hydrochloric acid in a gas-evolution bottle, with funnel for the addition of the acid, and two tubes, one for passing a current of air through the acid fluid, the other for conducting the gases through an alkaline solution of arsenious acid, coloured blue by litmus. In my first analysis, this alkaline solu-



tion was contained in two bottles, and as soon as the acid vapours had coloured the litmus red, the first bottle was removed, the second bottle put in place of the first, and a new bottle in the place of the second. All the sulphuretted hydrogen was driven out of the mass by boiling, and a current of air was passed through the fluid, and absorbed in the alkaline fluid. The united

solutions, on addition of an excess of hydrochloric acid, precipitated yellow flakes of a sulphur-compound of arsenic, which, collected on a filter, washed and dried, weighed 1·8 grains, corresponding to 0·743 grains of hydrosulphuric acid. On drying, this precipitate became brown and hard, and, on sublimation, yielded tersulphide of arsenic, as already stated, besides a quantity of charcoal. That so small a quantity of this sulphur-compound should have been obtained from about six ounces of gallstones is explained by the experience of Bolle, who analyzed two gallstones, only one of which yielded sulphuretted hydrogen.

The residue which remains after the removal of the hydro-

chloric acid extract, consists of cholochrome with traces only of the original admixtures.

The water-extract, on evaporation, yields a syrup, of a faintly acid reaction, mainly bile. It is soluble in water and spirits, and no crystalline organic compound is deposited from it, even after months of repose. But it has the remarkable property of holding in solution and at length depositing in well-defined, large crystals, phosphate of lime.

The alcoholic extract, on cooling, deposits a small quantity of white granular matter, which is collected on a filter, washed with alcohol, and dried. It consists of cholic acid, containing some fatty acid not easily separated. The filtrate has the property of amberggris, being amber in reflected, and green in transmitted light. It also has a most agreeable odour of musk. After a part of the alcohol has been distilled off, and the fluid has been again allowed to cool, flakes of crystalline matter are deposited. They probably consist of cholesterine. After further evaporation, a biliary acid is deposited in drops,—amorphous cholic acid. After prolonged standing, crystals of the same character as those obtained by alcohol from the deposit in rotten ox-bile are deposited,—crystallised cholic acid. Most of them are mixed with a syrup, from which they cannot be separated mechanically. This syrup is insoluble in water, and becomes resinous after contact with it: it has all the properties of choloidic acid. This mixture of acids is boiled for a long time with water, which dissolves cholic acid, and a light yellow matter,—perhaps choloidic acid, though this acid is reported to be quite insoluble in water. However that may be, the watery decoction, when left to spontaneous evaporation, which takes months, owing to the formation of a pellicle on the surface, at last deposits the very characteristic splendid needles of cholic acid, mixed with a granular brown deposit, which does not give the cholochrome reaction, and may be choloidic acid.

The hydrochloric acid extract is of a light brownish colour, and perfectly transparent. Evaporated on the water-bath, it deposits a black matter, which, after mixing with water, becomes brown, and consists of cholochrome, yielding the usual reaction. Several subsequent evaporations each yield some of this deposit, which ultimately becomes mixed with earths. The earths are phosphates of lime and magnesia, which are deposited in a crystalline state, when the solution, containing but little acid, is allowed to stand. By calcination they are freed from organic matter. Ultimately

there remains a saline mass, containing chloride of calcium, chloride of ammonium, and perhaps some traces of other matters yet to be ascertained.

The ingredients of ox-gallstones according to analyses upon the above plan, are the following: Bile, a residue of the fluid in which the concretions are formed. Cholochrome, cholic and choloidic acids, cholesterine, a sulphate in some cases, phosphates of lime and magnesia, carbonates of the same, and some ammonia-compounds, possibly a sulphate.*

Analysis of Putrid Ox Bile.

It is necessary to separate some of the white granules from the fluid, in order to show by combustion and treatment with acidulated ether, that they contain phosphate and palmitate or stearate of lime. The free fatty acid forms an emulsion on boiling with phosphate of soda.

The principal step in the analysis of this fluid, is the filtration and separation of the deposit. A bag of twilled calico is best used for that purpose. When the fluid has percolated, the smeary deposit in the bag must be kneaded with cold water, as otherwise it is impossible to wash it. When well washed, it is mixed with boiling alcohol, and boiled with it for some time; it is then again put in the washed calico bag. The filtrate on cooling deposits a large quantity of crystallized cholic acid. The mother-liquor on evaporation yields little cholic, and some choloidic acid. That part of the deposit which boiling alcohol did not dissolve, is well washed with alcohol, and extracted with a boiling solution of carbonate of potassa. This solution takes up the whole of the colouring matter, cholophaeine, and leaves behind a white mass of coagulated mucus, mixed with greenish crystals of phosphate of lime, which are separated by levigation. From the soda-solution, the cholochrome is obtained as the green modification, *cholocholine*, by precipitation with hydrochloric acid.

The deposit therefore is made up of stearate and palmitate of lime, cholic and choloidic acid, cholochrome, phosphate of lime in crystals, and mucus.

The port-wine-coloured fluid part of the bile is treated with sulphuric acid in slight excess: a large quantity of choloidic acid

* I may here allude to the discovery of sulphide of ammonium, which Lehmann states to have made, in the bile of a boy.

is then precipitated as a pitchy mass, which is easily soluble in warm alcohol, and contains but little cholic acid, deposited in crystalline granules after long standing of the alcoholic solution. The excess of sulphuric acid is removed, and any free acid neutralized by boiling the fluid residue with carbonate of baryta. When evaporated, this solution deposits resinous cholic acid (which does not decompose carbonate of baryta) to be extracted by alcohol. The alcohol causes a crystallization on standing with the fluid. The crystals consist of sulphate of soda, phosphate of soda, and taurine, to be separated mechanically, and in the ultimate mother-liquor of the decrystallized substances, some triple-phosphate is obtained, as also some chloride of ammonium, to be obtained pure by sublimation. The alcohol retains the acetate and valerate of ammonia, which salts, after evaporation of the alcohol, yield their acids on distillation with sulphuric acid. The addition of this latter acid still precipitates some resinous biliary matters.

The fluid part of putrid bile therefore contains choloidate of soda, a little cholate, a red colouring matter, perhaps cholochromic acid, taurine, valerate and acetate of ammonia, phosphate of soda, chloride of ammonium, and some other as yet undetermined matters.

Putrefaction and Analysis of Human Bile.

As human bile can only be obtained in quantity from persons who have died from disease, it will not easily afford the materials with which to repeat the experiments instituted with ox-bile, which is fresh, healthy, and normal. Human bile promiscuously collected in the dead-house, even allowing it to contain the normal ingredients, is mostly vitiated by a large amount of albumen, which enters the gall-bladder by endosmosis during the interval between death and obduction. This albumen coagulates in part during evaporation of such bile on the water-bath, another part remaining dissolved. If then such bile be subjected to putrefaction, the process takes place under different conditions, and yields therefore different results. This difference mainly consists in the circumstance, that the alkaline products of decomposition of albumen, either neutralize the acid products of the decomposition of bile, which would precipitate insoluble compounds, or dissolve them again should they have been precipitated. Deducting the products of the putrefaction of albumen, the products of the putrefaction of the bile

itself are the same as those obtained from ox-bile, although they are in a different form. Human bile is mostly neutral. When dissolved in alcohol, it parts with the mucus and albumen, and the filtrate, after evaporation of the alcohol, leaves a residue, which is entirely soluble in water, and such solution is neutral and not precipitated by oxalic or acetic acid. Sometimes however human bile exhibits an acid reaction; this on similar treatment with alcohol, and re-solution in water of the residue, yields a plastery precipitate of cholidic acid. When complete precipitation has been effected, the filtrate evaporated, and the concentrated fluid treated with alcohol, prismatic crystals of taurine are sometimes obtained. The solution always yields ammonia.

Human bile, which has been allowed to putrefy in a stoppered bottle, emits a horrible odour, is of a reddish brown colour, and apart from the deposit perfectly clear: it has an acid reaction. With acetic acid, it becomes troubled, and deposits a resinous precipitate; but the supernatant fluid remains thick, and does not become clear even on boiling and standing; the addition of hot alcohol resolves the turbidity.

XI.—*On some Derivatives from the Olefines.*

By FREDERICK GUTHRIE.

IV.

A CONSIDERABLE number of the substances whose formation and properties I have had the honour of describing to this Society in Memoirs I, II, and III, are non-volatile and uncrystallizable liquids. Hence, with regard to them, the two so-frequently adopted criteria of homogeneity are inapplicable; viz., constancy of boiling point and crystalline form. Although this want is shared by a vast number of bodies, both organic and inorganic—solid, liquid, and gaseous,—whose homogeneity is never called into question, yet additional evidence in this direction is not superfluous.

A method peculiarly applicable in such cases, is that of fractional

solution. It has been already successfully employed in determining the homogeneity of gases; and may be thus proposed. "When a solvent has partly dissolved a body, and the entire body has the same composition as either of the parts (dissolved or undissolved), or if the latter have the same composition as one another, then the original substance is simple or homogeneous."

No mixture can show this property unless its constituents are isomers or polymers of one another. The law itself enjoys, of course, nearly the same amount of truth as the proposition that no two substances are soluble to exactly the same extent, in the same medium, under the same conditions, unless the solubility of both be infinite.

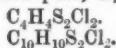
The inverse of the law is untrue to the extent that solution may effect decomposition.

The substances which I have submitted to this test are the two of the substances previously described, which seemed most prolific of derivatives; viz.,

*Bisulphochloride of ethylene $C_4H_4S_2Cl$.

*Bisulphochloride of amylene $C_{10}H_{10}S_2Cl$.

* M. Wurz (Répertoire de Chimie pure, ii, 337), in noticing these bodies and the two



remarks:—

" SCl_2 , corresponding to SO_2 , being diatomic, it follows that $SCl_2 - Cl$; that is, SCl , ought to be monatomic. Nevertheless, it is to be observed, that the constitution of these bodies may be regarded in another manner, by supposing them to contain the diatomic groups,—

Sulphide of ethylene ($C_4H_4S_2$)" and

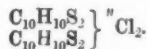
Sulphide of amylene ($C_{10}H_{10}S_2$)",

corresponding to the oxides. These groups, on combining with 2 atoms of chlorine, form the two following chlorides:—

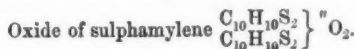
Dichloride of sulphethylene ($C_4H_4S_2$)" Cl_2 .

Dichloride of sulphamylene ($C_{10}H_{10}S_2$)" Cl_2 .

"As for the chloride $C_{10}H_{10}S_2Cl$, we double its equivalent, representing its constitution by the formula,—



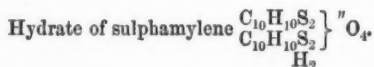
"It is known that 2 atoms of oxide of ethylene may unite, in order to combine with 1 atom of water. Hence, it is not extraordinary that 2 atoms of sulphide of amylene should join together in order to combine with 2 atoms of chlorine. If this way of looking at the matter is exact, we should represent the constitution of the oxide of disulphamylene and that of the hydrate of the oxide of disulphamylene by the formulæ—



The method was applied as follows:—A few grammes of the bisulphochloride of ethylene were warmed, with alcohol of about 85°, until nearly half dissolved. The alcoholic solution was then poured off, and the alcohol removed by evaporation on a water-bath, and washing with water. The product, after drying in *vacuo* over sulphuric acid, gave the results—

- I. 0.4436 gave 25.27%C, and 4.36H.
 II. 0.4280 gave 33.88%S.
 III. 0.2838 gave 36.00%Cl.

Comparing this with the analysis given before of the entire substance, we find,—



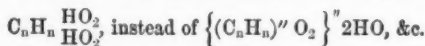
In reply, I would observe:—

1. That SCl_2 has not yet been formed; and that therefore speculations as to what its "atomicity" might be, are premature. Still more so must considerations be as to the effect which the withdrawal of chlorine would have on the hypothetical atomicity of this hypothetical body.

2. That, in such bodies as



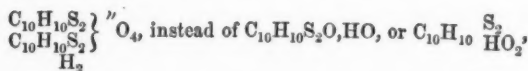
it seems preferable to suppose that the halogens are arranged in two "monatomic" groups, than to imagine, with M. Wurz, that there are two stages of saturation, each stage being a biatomic one. This, applied to glycols would give,—



3. Concerning the bodies,



I admit, in regard to some of their reactions, we have reason (neither more nor less) to double their formulæ than to double the formulæ of the ethers. But, to write the hydrated oxide of bisulphamylene,



is, I think, a useless complication. It does not represent the formation or properties of the body more clearly than the older formulæ; and moreover involves the idea of a "mixed type," which I have never been able to understand. But I must again insist here upon the uselessness of seeking to establish the formula of a body:—if formulæ of bodies at chemical rest are to express their potential recompositions. (See I.)

	$C_4H_4S_2Cl$ requires	Entire Substance	Dissolved Portion.
C	= 25.13	25.93	25.27
H	= 4.19	4.32	4.36
S	= 33.51	33.47	33.88
Cl	= 37.17	36.29	36.00
	<hr/> 100.00	<hr/> 100.01	<hr/> 99.51

About the same quantity of the bisulphochloride of amylene was treated in exactly the same manner. The dissolved portion, on analysis, gave the following results:—

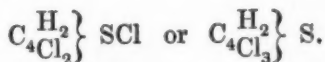
- I. 0.3934 grm. gave 23.81% S.
 II. 0.2677 „ gave 25.66% Cl.

Whence, comparing, as before, with the composition of the whole substance, we have,—

	$C_{12}H_{10}S_2Cl$ requires	Entire Substance.	Dissolved Portion.
C	= 43.64	43.80	„
H	= 7.27	7.47	„
S	= 23.27	23.93	23.81
Cl	= 25.82	24.73	25.66
	<hr/> 100.00	<hr/> 99.93	

Hence, it appears that, in both cases, the entire substance has virtually the same percentage composition as the dissolved portion; and accordingly, under the limitations above specified, the homogeneity of both bodies is established.

We have already seen the curious relation existing between the bisulphochloride of chlorethylene and the bisulphide of ethyl, in regard to the action on both of chlorine. The product in either case is the chlorosulphide of bichlorethylene or the sulphide of terchlorethyl.



This identity of product extends also to the bisulphochloride of ethylene. If a few grammes of the bisulphochloride of ethylene be exposed to a current of dry chlorine, the action being carried on for a few hours and assisted at last by the heat of a water-

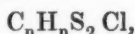
bath, a product is obtained, which after expulsion of the excess of chlorine by a current of carbonic acid, showed the following composition :—

- I. 0.3824 grm. gave 70.69 % Cl.
 II. 0.4380 grm. gave 10.63 % S.

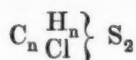
The sulphide of terchlorethylene requires

71.73 % Chlorine,
 10.63 % Sulphur.

So that the action of chlorine is to convert the bisulphochloride of ethylene, into the sulphide of terchlorethyl. *Towards chlorine*, therefore, bodies of the form



behave like sulphides of chloriferous radicles



inasmuch as the bisulphides of the radicles $C_n H_{n+1}$, give rise to the same products.

On treating $C_{10}H_{10}S_2Cl$ with oxide of lead, or with hydrate of potash, we have already seen the chlorine replaced by O and by HO_2 . Doubtless $C_4H_4S_2Cl$, would give rise to $C_4H_4S_2O$, on treatment with PbO . As yet I have only examined the action of hydrate of potash upon $C_4H_4S_2Cl$. If $C_4H_4S_2Cl$, and KOH , be both in alcoholic solution, the reaction between them on slightly warming is both immediate and complete. The KOH being employed in slight excess, and the filtrate from the precipitated KCl having been freed from alcohol by evaporation and washing with water, the hydrated bisulphoxide of amylene is obtained pure.

On analysis :

- I. 0.4333 gave 31.33 % C, and 6.67 % H.
 II. 0.2984 gave 42.26 % S.

$C_4H_4S_2OHO$ requires		I.	II.
C =	31.17	31.33	"
H =	6.49	6.67	"
S =	41.56	"	42.26
O =	20.78	"	"
<hr/>			
100.00			

The hydrate of bisulphoxide of amylene is a yellowish liquid of curious smell; like the body from which it is derived, it acts violently upon the mucous membrane. It dissolves in alcohol and ether, but is insoluble in water.

Further transformations intimately connected with the above, and with others previously described, are afforded by the replacement of the chlorine in



by cyanogen and sulphocyanogen. The method used in both cases, is similar to that employed for the oxygen and peroxide of hydrogen replacements, viz: digestion of the $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}$ with cyanide or sulphocyanide of potassium respectively, in alcoholic solution. The reaction is very neat. The precipitated chloride of potassium having been separated by filtration, the filtrate is evaporated on a water-bath, washed with water, and dried over sulphuric acid *in vacuo*.

Both products are liquids which can scarcely be distinguished by smell or other physical property. They have however evidently different densities. The first gave on analysis:

- I. 0.2432 gave 55.65 % C, and 7.60 % H.
 II. 0.3881 gave 24.66 % S.

$\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cy}$ requires			
		I.	II.
C =	56.25	55.65	"
H =	7.81	7.60	"
S =	25.00	"	24.66
N =	10.94	"	"
<hr/>			
100.00			

The specific gravity of this body is 1.07 at 13°C. Since there can be little doubt but that the sulphur and cyanogen in this substance are not in the same relation as in the sulphocyanides (for if so, S_4Cy_2 would be required to saturate $\text{C}_{10}\text{H}_{10}$), it is advisable to call the above body the *bithiocyanide* of amylene, rather than the "sulphocyanide" or "bisulphocyanide."

The product obtained by the action of the sulphocyanide of

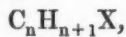
potassium upon the bisulphochloride of amylene, gave the following results on analysis:

- I. 0.2336 gave 44.46 C, and 6.54 H.
 II. 0.3768 gave 39.32 S.

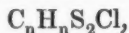
$C_{10}H_{10}S_2S_2Cy$ requires		I.	II.
C =	45.00	44.46	"
H =	6.25	6.54	"
S =	40.00	"	39.32
N =	8.75	"	"
<hr/>			
100.00			

The specific gravity of this body at 13°C is 1.16. The least ambiguous name which can be given to it is, perhaps, the *bithio-bithiocyanide* of amylene.

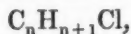
If we now compare the above and previously described behaviours of the bodies $C_4H_4S_2Cl$ and $C_{10}H_{10}S_2Cl$, with that of the halide of a radicle of the form



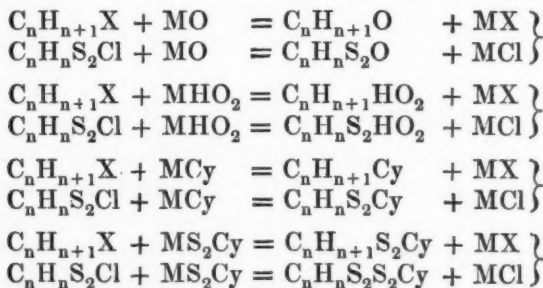
we must at once admit the parallelism of the recompositions in the two cases, and therewith admit that bodies of the form



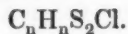
behave like the chlorides of the form



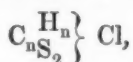
towards oxides, hydrated oxides, cyanides, and sulphocyanides.



Hence the rational formula of

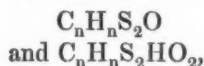


towards oxides, hydrated oxides, etc., may be written

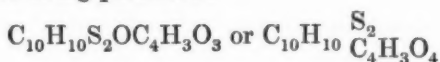


wherein we have the *chloride of a sulphuriferous radicle*: for in presence of these bodies, the sulphur and hydrocarbon remain together. We here then see a prominent example of the variations in the re-agent producing a corresponding variation in the rational formula.

According to this view, the bodies

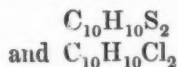


represent an ether and an alcohol. An additional argument for considering $\text{C}_{10}\text{H}_{10}\text{S}_2\text{HO}_2$ as an alcohol, will be found in the fact, that on dropping it into a large excess of strong sulphuric acid, which is kept cold, a conjugate acid is produced, having a soluble baryta-salt. This acid will be described subsequently. Again it would appear from a few experiments performed in this direction, that the peroxide of acetyl may replace the chlorine in $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}$, by the action of acetate of potash, the acetate of bisulphamylene being produced:



a body which is an analogue of acetic ether. Such derivatives must for the present be reserved.

The body $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}$, being thus prolific, it becomes important to examine the formation and properties of the bodies formed by the union of amylene with the separate halogens S and Cl, viz:



The first of these bodies, or the bisulphide of amylene, is easily obtained by the direct reduction of $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}$, by means of metallic zinc. Nascent hydrogen, which was at first tried, effects too profound a reduction, by withdrawing a portion of the sulphur. To prepare $\text{C}_{10}\text{H}_{10}\text{S}_2$, an ounce or two of $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}$ is dissolved in alcohol, and boiled for some hours with granulated zinc, the alcohol being condensed and allowed to flow back. The greater quantity of the alcohol is then distilled off, and the residue washed with water. A colourless liquid product collects on the surface of

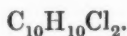
the water, which after washing and drying over chloride of calcium, may be rectified. It boils constantly at about 200°C.

- I. 0.8012 gave 30.60 % S.
- II. 0.2833 gave 58.32 % C, and 10.26 H.
- III. 0.3270 gave 58.26 % C, and 10.24 H.

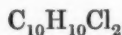
$C_{10}H_{10}S_2$ requires		I.	II.	III.	
C	= 58.82	„	58.32	58.26	58.29
H	= 9.80	„	10.26	10.24	10.25
S	= 31.38	30.60	„	„	30.60
<hr/>					<hr/>
100.00					99.14

The specific gravity of the bisulphide of amylene is 0.907 at 13°C.

Considerable difficulty attends the formation of bichloride of amylene.

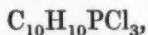


Amylene absorbs chlorine with the greatest eagerness; but when the two are brought together alone, as also when cold chlorine-water acts upon amylene, floating on its surface, large quantities of hydrochloric acid are formed, which points to the occurrence of some chlorhydrogen replacement. The formation of Dutch liquid by the action of pentachloride of antimony upon ethylene, suggested the possible formation of



by an analogous process.

Pentachloride of phosphorus was finely pounded and treated with perfectly dry amylene. No hydrochloric acid escaped, a few degrees of heat were evolved, and the whole became nearly dry. After having stood for twelve hours, the mass was placed in a basin and floated on water. At the end of another twelve hours, two layers were found, the lower consisting of phosphoric, and as experiment showed, phosphorous acid and hydrochloric acid,—the upper of bichloride of amylene. From the fact that the amylene and pentachloride of phosphorus produced in the first instance a solid, it would appear that the complementary PCl_3 re-united with the amylene to form the unstable body



which subsequently underwent decomposition. After washing

with water and drying, the upper layer was rectified. A product was thus obtained, which boiled at 141° – 147°C . On analysis:

- I. 0.2866 gave 42.22 % C, and 7.40 % H.
 II. 0.4279 gave 50.88 % Cl.

$\text{C}_{10}\text{H}_{10}\text{Cl}_2$ requires		I.	II.
C =	42.55	42.22	„
H =	7.09	7.40	„
Cl =	50.36	„	50.88
<hr/>			<hr/>
100.00			100.50

At 9°C . dichloride of amylene has the specific gravity 1.058.

It is not improbable that dichloride of amylene may give rise to bichloride of amylene, on treatment with cyanide of potassium. Bichloride of amylene may however be prepared in another and very singular manner.

It will be remembered that the gas NO_4 unites directly with amylene to form the body $\text{C}_{10}\text{H}_{10}\cdot 2\text{NO}_4$ (see III). This fact was used to support the view of NO_4 being a true halogen. The same conclusion is also suggested by the behaviour of $\text{C}_{10}\text{H}_{10}\cdot 2\text{NO}_4$ towards cyanide of potassium. If $\text{C}_{10}\text{H}_{10}\cdot 2\text{NO}_4$ be dissolved in alcohol at a gentle heat,* and added to an alcoholic solution of cyanide of potassium, an immediate precipitate is produced, which, after washing with alcohol and drying, gives a precipitate with nitrate of silver, soluble in nitric acid, and which, on treatment with sulphuric acid, gives an amount of sulphate of potash corresponding to the nitrite of potash (nitroxide of potassium). The alcoholic solution from the nitrite of potash is evaporated on a water bath, at about 60°C , until the greater portion of the alcohol is expelled. The residue is then repeatedly washed with small quantities of water, and dried over sulphuric acid in *vacuo*. The composition of the liquid product was found by analysis to be as follows:—

- 0.2760 gave 9.16 % of H.
 0.3500 gave 9.16 % of H, and 51.26 of C.
 0.3079 gave 16.00 % of N.

* An alcoholic solution of $\text{C}_{10}\text{H}_{10}\cdot 2\text{NO}_4$ is decomposed on boiling. Chloroform dissolves $\text{C}_{10}\text{H}_{10}\cdot 2\text{NO}_4$ abundantly, as also does glacial acetic acid. Strong sulphuric acid instantly decomposes it.

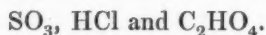
$C_{10}H_{10}Cy_2 + 5HO$ requires		I.	II.	III.
C	= 50.30	,,	51.26	,,
H	= 8.98	9.16	9.16	,,
N	= 16.77	,,	,,	16.00
<hr/>				<hr/>
76.05				76.42

The body according to this analysis, is the pentahydrate of bicyanide of amylene. The water attached to the cyanide is to be compared to water of crystallization. It is given off on heating the hydrate, but remains combined when the hydrate is exposed for any time over sulphuric acid. It may be sufficient here to notice—(1) That five equivalents of water would be essential to the conversion of the cyanide of amylene into pimelate of potash by the action of caustic potash. (2) That my few experiments to prepare pimelate of potash from the cyanide have not been successful.

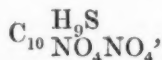
The binitroxide of amylene appears also to exchange its NO_4 for O, HO_2 S, and S_2Cy . Most of these bodies will probably be soon described by those chemists who are engaged in researches on the diatomic alcohols.*

A body intimately connected, on the one hand, with $C_{10}H_{10}2NO_4$, and, on the other, with the chlorine-derivatives of $C_{10}H_{10}S_2Cl$, is the product of the action of $HO.NO_5$ upon $C_{10}H_{10}S_2Cl$.

On warming $HO.NO_5$ with $C_{10}H_{10}S_2Cl$, a tempestuous, and, in some respects, complicated, reaction is established. One phase of the reaction results in the formation of the products,



showing that a part of the $C_{10}H_{10}S_2Cl$ has suffered complete disorganisation. Moreover, a copulated sulphuric acid is formed, which has a soluble baryta-salt, but has not been further examined. The other, and more easily applicable reaction, is the formation of



or, the nitrosulphide of nitroxamylene.

* Dr. Simpson's preparation of cyanide of ethylene, and thence of succinate of potash, will, I expect, on publication of his analyses, throw light on this subject.

It is this body which appears in the distillate when $C_{10}H_{10}S_2Cl$ is warmed in a retort with $HO.NO_5$, as a heavy liquid of green colour, insoluble in water. After washing with water and drying, it is pure.

grms.
 0·2579 gave 34·82%C and 4·82%H.
 0·2620 gave 34·26%C and 5·25%H.
 0·1838 gave 9·39%S

$C_{10}H_9S_2NO_4$ requires.	I.		
C = 33·89	34·82	34·26	„
H = 5·08	4·82	5·25	„
S = 9·04	„	„	9·39

The nitroxisulphide of nitroxamylene is soluble in ether and alcohol, and suffers, apparently, very easy reduction by sulphide of ammonium.

Before leaving this part of the subject, it may be in place to offer a view connecting the two nitroxiolefines described with some known bodies. Such connection at once appears on looking at the following list, which might be much extended.

Example.

C_nH_n , or $C_nH_n\{C_nH_n$ Olefiant gas.

$C_nH_n\left\{\begin{smallmatrix} C_nH \\ H \end{smallmatrix}\right.{}^{n+1}$ Ethyl.

$C_nH_n\left\{\begin{smallmatrix} Z_n \\ H \end{smallmatrix}\right.$ Zinc-ethyl.

$C_nH_n\left\{\begin{smallmatrix} C_mH \\ H \end{smallmatrix}\right.{}^{m+1}$ Ethyl-amyl.

$C_nH_n\left\{\begin{smallmatrix} H \\ H \end{smallmatrix}\right.$ Hydride of ethyl.

$C_nH_n\left\{\begin{smallmatrix} H \\ Cl \end{smallmatrix}\right.$ Chloride of ethyl.

$C_nH_n\left\{\begin{smallmatrix} Cl \\ Cl \end{smallmatrix}\right.$ Dutch liquid.

$C_nH_n\left\{\begin{smallmatrix} H \\ O \end{smallmatrix}\right.$ Ether.

$C_n H_n \left\{ \begin{smallmatrix} H \\ HO_2 \end{smallmatrix} \right.$	Alcohol.
$C_n H_n \left\{ \begin{smallmatrix} O \\ O \end{smallmatrix} \right.$	Ethylenic ether.
$C_n H_n \left\{ \begin{smallmatrix} HO_2 \\ HO_2 \end{smallmatrix} \right.$	Glycol.
$C_n H_n \left\{ \begin{smallmatrix} NO_4 \\ NO_4 \end{smallmatrix} \right.$	Binitroxide of anylene.
$C_n H_{n-1} NO_4 \left\{ \begin{smallmatrix} S \\ NO_4 \end{smallmatrix} \right.$	Nitroxisulphide of nitroxamylene.
$C_n H_n \left\{ \begin{smallmatrix} SO_3 \\ SO_3 \end{smallmatrix} \right.$	"Sulphate of carbonyl."
$C_n H_n \left\{ \begin{smallmatrix} H \\ NO_4 \end{smallmatrix} \right.$	Glycocine.

To which might be added the much-formulized acid series:—

$C_n H_{n-2} \left\{ \begin{smallmatrix} HO_2 \\ HO_2 \end{smallmatrix} \right.$	Hydrated acetic acid.
$C_n H_{n-2} \left\{ \begin{smallmatrix} HO_2 \\ O \end{smallmatrix} \right.$	Acetic anhydride.

A series such as the above may assert a claim rather as a device for classification than as a method of accomplishing what most formulæ profess to perform, viz., an index to molecular arrangement.

To many of what are called homologous series, methylene plays the same part chemically as the common difference plays in an arithmetic series. Hence the question forces itself upon us: Is it possible, by means of the successive chemical additions of methylene, to advance from an inferior to any superior term of such a homologous series?

The doubt as to the existence of methylene, and even, in the eyes of some, as to the possibility of its existence, puts a practical end to this question at present.

A moment's consideration shows that the successive formation of all higher terms could be effected by means of ethylene, provided *two* consecutive homologous terms were taken, that is, terms differing by methylene.

Further, by means of propylene, we could effect the same

purpose, provided that *three* consecutive homologous terms were at our disposal to begin with. And so *mutatis mutandis* for the other olefines.

The suggestion as to the possibility of this method of building up was already given in Memoir I, wherein the action of zinc-ethyl upon $C_{10}H_{10}S_2Cl$ was suggested. The subsequent experiments which have been described as to the easy replacement of the Cl in $C_{10}H_{10}S_2Cl$ by other halogens only confirmed this idea. In zinc-ethyl, as far as it consists of zinc and ethyl, the ethyl is the halogen. Can, then, the ethyl from zinc-ethyl be made to replace the chlorine $C_nH_nS_2Cl$? and what relation will the body thus produced bear to the bisulphide of ænanthyl?



If an excess of ethereal solution of zinc-ethyl (as it comes from the digester) be allowed to fall upon the bisulphochloride of amylenes, considerable heat is developed. It is best to allow the heat to moderate itself by the evaporation of the ether, and not to cool artificially. Two layers are formed. These are treated separately with water, the oil which floats on the surface is taken off, and the solid body (oxide of zinc) is exhausted with alcohol. The alcoholic solution and the oil are mixed, freed from alcohol by gentle evaporation, washed with water, dried and rectified. The product boils almost constantly at about 240° – $250^{\circ}C$. It gave, on analysis,

0.2730 gave 65.31% C and 11.22 H,

0.4152 gave 65.4% C and 11.26 H.

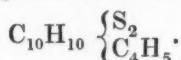
0.4186 gave 23.72% S

$C_{14}H_{15}S_2$ requires		I.	II.	III.
C	64.12	65.31	65.42	„
H	11.46	11.22	11.26	„
S	24.42	„	„	23.72
<hr/>				<hr/>
100.00				100.32

so that the product has, in fact, the percentage-composition of bisulphide of ænanthyl.

Although I believe by this means to have found the key to the problem of the successive synthesis of ascending terms of a homo-

logous series; it will be more generally acceptable if the above body be termed, for the present, the bisulphethide of amylene.



An examination of the products of recomposition of this and similar bodies I reserve for a future communication.

The bodies which I have had the honour of bringing before the notice of the Society in this and previous Memoirs, are the following :—

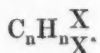
From Ethylene.

$\text{C}_4\text{H}_4\text{S}_2\text{Cl}$	Bisulphochloride of ethylene.
$\text{C}_4\text{H}_4\text{S}_2\text{Cl}_2$	Bichlorosulphide of ethylene.
(a) $\text{C}_4\text{H}_2\text{SCl}_3$	Chlorosulphide of bichlorethylenc.
(β) $\text{C}_4\text{H}_2\text{SCl}_3$	Sulphide of terchlorethyl.
$\text{C}_4\text{H}_4\text{S}_2\text{HO}_3$	Hydrate of bisulphoxide of ethylene.

From Amylene.

$\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}$	Bisulphochloride of amylene.
$\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cl}_2$	Bichlorosulphide of amylene.
$\text{C}_{10}\text{H}_7\text{SCl}_4$	Chlorosulphide of terchloramylene.
$\text{C}_{10}\text{H}_{10}\text{S}_2\text{O}$	Bisulphoxide of amylene.
$\text{C}_{10}\text{H}_{10}\text{S}_2\text{HO}_2$	Hydrated bisulphoxide of amylene.
$\text{C}_{10}\text{H}_9\text{S}_2$	Bisulphide of fusyl.
$\text{C}_{10}\text{H}_{10}\text{S}_2$	Bisulphide of amylene.
$\text{C}_{10}\text{H}_{10}\text{Cl}_2$	Bichloride of amylene.
$\text{C}_{10}\text{H}_{10}\text{Cy}_2 + 5\text{HO}$	Penthydrated bicyanide of amylene.
$\text{C}_{10}\text{H}_{10}\text{S}_2\text{Cy}$	Bithiocyanide of amylene.
$\text{C}_{10}\text{H}_{10}\text{S}_4\text{Cy}$	Bithiosulphocyanide of amylene.
$\text{C}_{10}\text{H}_{10}\cdot 2(\text{NO}_4)$	Binitroxide of amylene.
$\text{C}_{10}\text{H}_9\text{S}\cdot 2(\text{NO}_4)$	Nitroxisulphide of nitroxamylene.
$\text{C}_{10}\text{H}_{10}\text{S}_2\text{C}_4\text{H}_5$	Bisulphide of ænanthyl.

The above are, of course, merely the equivalent formulæ. The formulæ of all these compounds are on the type



XII.—*On the amount of Water displaced from the Hydrates of Potash, Soda, and Baryta by Boracic and Silicic Acids.*

By CHARLES L. BLOXAM.

IN a communication which was printed in the Society's Journal of July, 1859, I described a series of experiments upon the action of boracic acid on the carbonates of the alkalies and alkaline earths at high temperatures, from which it appeared, that, at a bright-red heat, one equivalent (34.9) of that acid is capable of expelling from carbonate of potash, one equivalent (22) of carbonic acid, from carbonate of soda, two equivalents; from carbonate of lithia, two and a half equivalents; from carbonate of baryta, two and a half equivalents; and from carbonate of strontia, three equivalents of carbonic acid.

It would be inferred, from these results, that one equivalent of boracic acid is capable of combining with three equivalents (and perhaps even with more) of a basic oxide of the type MO, and that its capacity for bases could not be fully satisfied by its action upon the carbonates of the more powerful bases, on account of the energy with which they retained their carbonic acid.

It might be expected that since the water is more easily expelled from the hydrates, than the carbonic acid from the carbonates, the former would allow the boracic acid to satisfy its capacity for bases far more readily, and it might be hoped that a limit would be found to the displacing power of this acid for water.

In the experiments made to determine this question with the hydrates of potash and soda, fair specimens of the fused hydrates were heated to dull redness in a silver tray enclosed in a glass tube, through which a current of air was drawn by an aspirator, the air having traversed, before entering the tube, a wash-bottle with strong potash, a wash-bottle with oil of vitriol, a U-tube with fragments of fused potash, and a second U-tube with pumice and oil of vitriol. The composition of the hydrates fused under these circumstances until of constant weight, having been carefully determined, fresh quantities were fused in the tray and weighed in the corked tube, at intervals of ten or fifteen minutes, until their weight ceased to vary to any important extent. A weighed quantity of freshly fused boracic acid was then introduced as

rapidly as possible, the tube and its contents being again weighed, in case a little water or carbonic acid should have been absorbed from the air. Heat was then gradually applied to the tube, and the boracic acid fused with the hydrate, in the current of pure and dry air, until the weight of the (corked) tube and its contents ceased to vary to any extent capable of affecting the result of the experiment. At the conclusion, the temperature was always high enough to soften the hard glass tube, an Argand gas-lamp being employed, and a hood of sheet platinum being placed over the heated part of the tube.

Since, in this way, the boracic acid was allowed to act upon the same sample of hydrated alkali, which had already been subjected to the same conditions until it ceased to lose weight, any loss which was suffered during the fusion with the boracic acid must represent the amount of water displaced from the hydrate by that acid.

In many of the experiments, a weighed chloride of calcium tube was introduced between the fusion-tube and the aspirator, and after this had ceased to gain any water from the fused hydrate alone, the boracic acid was introduced and the experiment continued until the drying tube suffered no increase of weight.

The gain of the chloride of calcium tube was found to correspond almost exactly with the loss of the fusion-tube.

Action of Boracic Acid upon Hydrate of Potash at a red heat.

A somewhat unexpected difficulty arose in the course of these experiments, from the tendency of the fused hydrate of potash to absorb oxygen when heated in a current of air.

When 50 grains of the hydrate, which had been heated to fusion in the silver tray, and maintained in fusion for half an hour in the stream of dry and pure air, were allowed to cool, and dissolved in water, 0.4 cubic inch of oxygen escaped with rapid effervescence, and grey spangles of silver separated. The loss suffered by the silver tray in the course of the experiment amounted to 0.14 grn., and the corrosion of the tray was evident, soon after the commencement of the fusion, from the appearance of lustrous spangles of silver in the clear fused hydrate.

The fused masses obtained with hydrate of potash and boracic acid effervesced very rapidly with water, from the evolution of oxygen, and allowed inky black flakes to separate, which appeared to be simply silver in a finely divided state.

In order to ascertain to what extent this absorption of oxygen would interfere with the determination of the amount of water displaced by the boracic acid, the tube containing the fused mass was heated until its weight was very nearly constant, and a weighed drying tube was then attached to the fusion-tube; on continuing the application of heat for half an hour, in a current of dry and pure air, the fusion-tube with the hydrate had lost only 0.02 grn., whilst the drying tube had gained 0.17 grn. of water, showing that the absorption of oxygen by the fused hydrate was attended by a disengagement of water. On dissolving the fused mass in water, 0.5 cubic inch of oxygen was collected, the weight of which would be 0.17 grn., so that it would have exactly counterbalanced the loss of water. Doubtless the oxygen absorbed is not exactly equal to the water expelled; but it was proved by several experiments that the difference between the two weights was not sufficient to affect the result of the experiment.

In no case of the fusion of boracic acid with hydrate of potash, was more than 0.5 cubic inch of oxygen disengaged when the mass was dissolved in water.

In order to ascertain the composition of the specimen of hydrate of potash employed, and to prove that when subjected to the conditions of the experiment, the potash remained in combination with a single equivalent of water, the following experiments were made.

1. 29.16 grns. of a good specimen of the fused hydrate were fused, in the silver tray, in a current of pure dry air, for fifteen minutes, till the hydrate began to volatilise slightly. The loss amounted to 3.56 grns. or 12.2 per cent., representing the extraneous water. On further heating for ten minutes, it gained 0.03 grn.

25.04 grns. of this fused mass, dissolved in water, and the carbonic acid determined in Fresenius and Will's apparatus, gave 0.8 grn. carbonic acid, or 3.19 per cent.

2. 27.96 grns. of the hydrate which had been fused till it ceased to lose weight, were dissolved in water, and the total amount of available alkali determined by neutralising with hydrochloric acid of known strength. The (alkaline) potash present amounted to 22.79 grns. or 81.5 per cent. Deducting from this the weight of potash required to combine with the carbonic acid, viz. 6.8 grns., there are left 74.7 grns. of potash present as hydrate, which would give 89.0 per cent. of hydrate of potash.

The solution neutralised with hydrochloric acid was evaporated to dryness, the residue ignited and weighed; it gave 36.64 grns., which contained 0.37 grn. of sulphate of potash, and 0.36 grn. of chloride of calcium, leaving 35.91 grns. of chloride of potassium, representing 22.65 grns. of potash, or 81.0 per cent. Deducting from 100 parts of the hydrate, the sum of the constituents thus determined (viz.: potash, carbonic acid, sulphate of potash, and lime), amounting to 85.24 grns., there are left 14.76 grns. to represent the water of hydration. The amount of water required by theory to combine with the 74.7 of potash present as hydrate, would be 14.3 grns.

Since the sample contained small quantities of alumina, silica, and chloride of potassium, it may fairly be concluded that one equivalent of potash was combined in the fused hydrate with one equivalent of water.

The hydrate of potash fused till it ceased to lose weight, contained therefore, in 100 parts,

Hydrate of potash	89.00
Carbonate of potash	9.99

with a little lime, alumina, sulphuric acid, silica, and chlorine.

Three experiments were made upon the action of boracic acid on the hydrate of potash, with the results exhibited in the subjoined table.

	Actual weights in grains.			Number of equivalents.*		
	Boracic Acid.	Hydrate of Potash†.	Water expelled.	Boracic Acid.	Hydrate of Potash.	Water expelled.
I.	9.92	41.90	5.01	1	2.60	1.96
II.	9.28	41.69	4.75	1	2.70	1.98
III.	4.96	31.78	2.59	1	3.98	2.02

In the last experiment, the air, after leaving the tube in which the fusion was conducted, passed through a bottle containing lime-water, which gave not the least indication of the presence of carbonic acid.

The mean of the last two experiments would give exactly two equivalents (18) of water displaced by one equivalent (34.9) of boracic acid from an excess of hydrate of potash.

* Equivalent of boracic acid = 34.9; hydrate of potash = 47; water = 9.

† Calculated from the result of the preliminary analysis.

Action of Boracic Acid upon Hydrate of Soda at a red heat.

Hydrate of soda attacked the silver tray very slightly, its weight, in some experiments, not having perceptibly diminished; and the fused mass evolved hardly a trace of gas when dissolved in water.

The sample of hydrate of soda employed, when fused till its weight was constant, lost 1.27 per cent. of extraneous water.

The hydrate thus freed from water, was analysed, as in the case of hydrate of potash, and was found to contain, in 100 parts,

Hydrate of soda	90.41
Carbonate of soda	4.02

with a little alumina, silica, lime, chlorine, and sulphuric acid.

The subjoined table exhibits the results of three experiments upon the action of boracic acid on the hydrate of soda.

Actual weights in grains.			Number of equivalents*.			
	Boracic Acid.	Hydrate of Soda.†	Water expelled.	Boracic Acid.	Hydrate of Soda.	Water expelled.
I.	4.89	31.91	3.77	1	5.6	2.98
II.	4.46	35.78	3.43	1	7.0	2.98
III.‡	2.67	"	2.10	1	"	3.04

The mean of these experiments would give exactly three equivalents (27) of water displaced by one equivalent (34.9) of boracic acid from an excess of hydrate of soda.

Action of Boracic Acid upon Hydrate of Baryta at a red heat.

Since it was proved by experiments described in a former communication‡ that hydrate of baryta when fused in a silver crucible till of constant weight is represented by the formula BaO.HO , the experiments upon the quantity of water displaced from it by boracic acid were made in a closed silver crucible.

Crystallised hydrate of baryta, the purity of which had been ascertained by a quantitative analysis, was effloresced in vacuo over oil of vitriol, until it was converted into the compound $\text{BaO.HO} + \text{Aq.}\S$. The proportion of water having been verified by direct

* Equivalent of soda = 31

† Calculated from the result of the preliminary analysis.

‡ A fresh quantity of boracic acid was added to the fused mass in II, and the experiment continued.

§ Quarterly Journal Chem. Soc. April, 1860.

experiment, a weighed quantity of the hydrate was rapidly and intimately mixed with a weighed quantity of pure boracic acid dried at 212° Fah., which had been previously shown to have the composition $\text{HO} \cdot \text{BO}_3$.

The crucible was then covered and heated until it ceased to lose weight. By subtracting from the loss of weight suffered by the contents of the crucible, the weight of water known to be expelled by heat from the effloresced hydrates of baryta and boracic acid, the amount of water really displaced from the hydrate of baryta by the boracic acid was inferred.

In the following table, the results of four experiments of this description are recorded.

Actual weight in grains.			Number of equivalents*.		
Boracic Acid ($\text{HO} \cdot \text{BO}_3$).	Hydrate of Baryta ($\text{BaO HO} + \text{Aq.}$)	Water expelled.	Boracic Acid.	Hydrate of Baryta.	Water expelled†.
I. 3.17	27.36	5.36	1	4.00	2.92
II. 3.00	22.93	4.86	1	3.55	3.12
III. 2.51	21.60	4.17	1	4.00	3.11
IV. 2.96	25.47	4.87	1	4.00	3.03

From the mean of these experiments, it appears that almost exactly three (3.045) equivalents (27) of water are displaced by one equivalent (34.9) of boracic acid from an excess of hydrate of baryta.

If the equivalent of boracic acid be taken as 34.9, it displaces, from hydrate of potash, two equivalents, and from the hydrates of soda and baryta, three equivalents of water. Now, it was found in the experiments cited above, that one equivalent of boracic acid displaced only two and a half equivalents of carbonic acid from the carbonate of baryta, though it displaced three equivalents from the carbonate of strontia, which stands in the same position with respect to the carbonates, as hydrate of baryta does to the hydrates, that is, the next in the series of carbonates (carbonate of lime) is decomposable by heat alone, just as hydrate of strontia (the next in the series of hydrates).

If it be granted that the water in hydrate of baryta is more easily displaced than that in hydrate of soda, it follows that since boracic acid displaces no more water from the former than from the latter, its capacity for bases must be satisfied by the three equivalents of soda or baryta with which it then combines, as by

* Equivalent of baryta = 76.5.

† After deducting that due to the materials.

the three equivalents of strontia with which it combined when heated with the carbonate.

If the number 34.9 be retained for the equivalent of boracic acid, it must therefore be regarded as a tribasic acid; a view which may be thought to receive some support from the following considerations.

Boracic ether is represented, upon the ethyl hypothesis, as $3C_4H_5O \cdot BO_3$, and its analogues in the methyl and amyl series have a similar composition. Crystallised boracic acid has the formula $3HO \cdot BO_3$. Borate of magnesia, obtained by Rammelsberg by boiling a solution of borax with sulphate of magnesia, had the composition $3MgO \cdot BO_3$. Octohedral borax, and common borax dried at $212^\circ F.$, have the composition $NaO \cdot 2BO_3 + 5HO$, which may be represented as a tribasic salt if the water be considered to play the part of a base.

The biborate of potash, according to Laurent, has a similar composition $KO \cdot 2BO_3 + 5HO$. A terborate of potash, obtained by Laurent, had the composition $KO \cdot 3BO_3 + 8HO$, which would also be a tribasic salt if the water were admitted into the formula.

The tendency of boracic acid to form acid salts and double salts, is not observed in acids which are undeniably monobasic.

Action of Silicic Acid upon Hydrate of Potash at a red heat.

The experiment was conducted in exactly the same manner as in the case of boracic acid. The fused mass of silicate of potash dissolved, in every case, entirely in water, with the exception of a few white lustrous flakes of silver, disengaging oxygen with rapid effervescence. The largest quantity of oxygen disengaged (from a mass containing 40 grains of hydrate of potash, which had been fused for about an hour, in all) was 0.9 cub. in., which would weigh 0.31 grn., and would be at least partly compensated for (as shown by the experiment previously cited) by a corresponding displacement of water from the fused hydrate.

The annexed table contains the results of four experiments.

	Actual weights in grains.			Number of equivalents.*		
	Silicic Acid.	Hydrate of Potash†.	Water expelled.	Silicic Acid.	Hydrate of Potash.	Water expelled.
I.	4.65	31.46	2.15	1	3.6	1.54
II.	4.64	41.23	2.26	1	4.7	1.62
III.	5.20	32.17	2.44	1	3.3	1.45
IV.	4.97	31.24	2.29	1	3.3	1.53

* Equivalent of silicic acid (SiO_2) = 30.

† Calculated from the result of the preliminary analysis.

The silicic acid used in these experiments had been prepared by the fusion of sand with carbonate of soda, and carefully purified from all soluble ingredients by the usual processes.

It appears from these experiments that the proportion of water expelled increases, to a slight extent, with the proportion of hydrate of potash employed; but if the mean of experiments I, III, and IV be taken, we have almost exactly 1.5 eqs. (13.5) of water displaced by one equivalent (30) of silicic acid from an excess of hydrate of potash at a red heat*

Action of Silicic Acid upon Hydrate of Soda at a red heat.

The same specimen of silicic acid was used for these experiments, together with the hydrate of soda employed in the case of boracic acid.

	Actual weights in grains.			Number of equivalents.		
	Silicic Acid.	Hydrate of Soda†.	Water expelled.	Silicic Acid.	Hydrate of Soda.	Water expelled.
I.	4.83	35.75	2.94	1	5.5	2.02
II.	4.91	34.04	3.03	1	5.2	2.05

These results indicate that almost exactly two equivalents (18) of water are displaced by one equivalent (30) of silicic acid from an excess of hydrate of soda at a red heat.*

Action of Silicic Acid upon Hydrate of Baryta at a red heat.

The experiments with hydrate of baryta and silicic acid were attended, as might be expected, with more difficulty, partly from the want of fusibility of the silicate of baryta, and partly from the disparity in the equivalent numbers of these bodies.

The first three experiments in the table were made in a covered silver crucible, and the fourth in the silver tray, heated in a current of dry and pure air.

In experiments II and III, the silicic acid (in II, prepared from sand, in III pure rock-crystal) was mixed with effloresced hydrate of baryta, the extraneous water having been determined by preliminary analysis, and allowed for in the calculation.

In I and IV, the hydrate of baryta was fused till it ceased to

* Col. Yorke found that 30 parts of silicic acid expelled 8.76 of water (0.97 eqs.) from hydrate of potash, and 15.7 of water (1.74 eqs.) from hydrate of soda, the fusion being effected in a deep crucible.

† Calculated from the preliminary analysis.

lose weight, the silicic acid then added, and the fusion continued till no further loss was perceived.

The fused mass, in every case, gelatinised when treated with dilute hydrochloric acid.

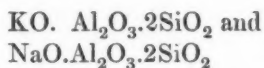
	Actual weights in grains.			Number of equivalents.		
	Silicic Acid.	Hydrate of Baryta (BaO.HO).	Water expelled.	Silicic Acid.	Hydrate of Baryta.	Water expelled.
I.	1.97	21.30	1.09	1	3.8	1.84
II.	3.31	30.47	1.83	1	3.2	1.85
III.	3.61	30.49	1.97	1	3.0	1.82
IV.	2.85	31.78	1.61*	1	3.9	1.88

It may, I hope, be fairly inferred from these experiments, that one equivalent (30) of silicic acid does not displace more than two equivalents (18) of water from hydrate of baryta at a red heat.

Silicic acid then, like boracic, appears to have satisfied its capacity for bases in its action upon hydrate of soda, when it combines with two equivalents of that alkali, since it refuses to displace a larger proportion of water from the hydrate of baryta. If the formula SiO_2 (= 30) be accepted for silicic acid, it would be a bibasic acid, a conclusion to which the following considerations lend some support.

The disilicate of ethyl has the formula $2\text{C}_4\text{H}_5\text{O.SiO}_2$. The ordinary specimens of crystallised finery-cinder and of the slag from copper-smelting furnaces (melting for coarse metal), have the composition 2FeO.SiO_2 . It is also commonly asserted that the most fusible slag from the blast furnace is that in which the oxygen contained in the bases equals that in the silicic acid, which is the case in silicates of the bibasic type (2MO.SiO_2).

Berzelius obtained the salts—



which are obviously bibasic, since Al_2O_3 is equivalent to 3MO .

Scheerer† has recently found that 30 parts of silicic acid fused with a large excess of carbonate of soda at a high temperature, expel 44 parts of carbonic acid. Col. Yorke had previously

* Increase of weight of the chloride of calcium tube. The loss of weight suffered by the fusion tube was 1.63, which would give 1.91 eqt. of water displaced by 1 eqt. of silicic acid. On the supposition that 1 eqt. of SiO_2 had displaced 2 eqs. HO, the actual weight of the water should be 1.71 grns.

† Ann. Ch. Pharm. cxvi. 129.

shown that 30 parts of silicic acid expelled 44 parts of carbonic acid from carbonate of lithia at a high temperature.

The disposition of silicic acid to form acid salts and double salts does not belong to a monobasic acid.

The formulæ of some of the chief natural silicates constituted upon a bibasic type are here given.

Villarsite	$2(2\text{MgO}.\text{SiO}_2) + \text{Aq.}$
Batrachite	$2\text{CaO}.\text{SiO}_2 + 2\text{MgO}.\text{SiO}_2^*$
Cerite	$2\text{CeO}.\text{SiO}_2 + 2\text{Aq.}$
Bucholzite	$2\text{Al}_2\text{O}_3.3\text{SiO}_2$
Pholerite	$2\text{Al}_2\text{O}_3.3\text{SiO}_2 + \text{Aq.}$
Vesuvian	$3\text{MO}.\text{M}_2\text{O}_3.3\text{SiO}_2^\dagger.$
Garnet	$3\text{MO}.\text{M}_2\text{O}_3.3\text{SiO}_2$
Scapolite } Anorthite }	$\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$
Sodalite	$3(\text{NaO}.\text{SiO}_2 + \text{Al}_2\text{O}_3.\text{SiO}_2) + \text{NaCl.}$
Zircon	$2\text{ZrO}.\text{SiO}_2$
Phenakite	$2\text{GIO}.\text{SiO}_2$
Helvine	$\text{GIO}.\text{MnO}.\text{SiO}_2$
Hydrosilicate of manganese	$2\text{MnO}.\text{SiO}_2 + 2\text{Aq.}$
Karpholite	$\text{MnO}.\text{Al}_2\text{O}_3.2\text{SiO}_2 + 2\text{Aq.}$
Electric Calamine	$2\text{ZnO}.\text{SiO}_2 + \text{Aq.}$
Hyalosiderite	$4\text{MgO}.2\text{FeO}.3\text{SiO}_2.$
Knebelite	$\text{MnO}.\text{FeO}.\text{SiO}_2$
Cyanite	$2\text{Al}_2\text{O}_3.3\text{SiO}_2$ (Klaproth).
Hisingerite	$\text{FeO}.\text{Fe}_2\text{O}_3.2\text{SiO}_2 + 6\text{Aq.}$
Olivine	$2(\text{MgFe})\text{O}.\text{SiO}_2$

Several points of resemblance between carbon, boron, and silicon, as well as between their acids, lead many chemists to associate them as a natural group. But the atomic weights (6, 10.9, and 14) do not exhibit any such simple numerical relation as is frequently to be traced in other groups of elements presenting similar analogies.

If the group BO_3 which appears by the above experiments, to

* According to Mitscherlich, many furnace slags, having the crystalline form of olivine have the same composition as batrachite (Gmelin).

† MO representing CaO , FeO , MnO , or MgO , and M_2O_3 , Fe_2O_3 or Al_2O_3 .

represent 3HO , be supposed really to contain 3 atoms of boracic acid, the atomic weight of the latter would be $\frac{34.9}{3}$ or 11.6 and that of boron, 3.6.

Again, if SiO_2 be supposed to represent 2 atoms of silicic acid, the atomic weight of the latter would be $\frac{30}{2}$ or 15, and that of silicon 7.

The atomic weights of the three elements would then be

Boron	3.6
Carbon	6
Silicon*	7

The atomic weight of boron added to twice that of silicon, would then give (17.6) nearly thrice that of carbon.

If boracic acid be regarded as BO_2 , the atomic weight of boron would be 7.3, or almost exactly half that assigned by Berzelius to silicon (14.8).

According to this view, the numbers would be

Carbon	6
Boron	7.3
Silicon	14.8

an arrangement more in accordance with our knowledge of the gradations observed in the properties of carbonic, boracic, and silicic acids, such as their displacing power over water, their physical states, solubility, acid character, &c.

XIII.—*On some Minerals from Chile.*

By FREDERICK FIELD.

A SHORT paper published in the Journal of this Society (Vol. xii, p. 8) on some minerals containing arsenic, sulphur, and copper from Chile, was concluded by the observation that I was then engaged in the investigation of a mineral containing sulphur, antimony, copper, and iron, with small quantities of silver, the ore being thickly sprinkled with bisulphide of iron: no specimen could

* If the atomic weight of silicic acid be taken, according to Berzelius, as 30.3, that of silicon, upon the above hypothesis, would be 7.2; or, if that given by Pelouze (30.2) be employed, the atom of silicon would be 7.1, almost exactly double that of boron.

be obtained pure enough for analysis. After much time had been bestowed upon this substance, no formula could be deduced, as the iron pyrites seemed to be intimately blended with the mineral itself. The discovery of the compound $\text{Cu}_2\text{S}, \text{AsS}_3$ analogous to the beautiful silver mineral AgS, AsS_3 rendered it very interesting to find a corresponding $\text{Cu}_2\text{S}, \text{SbS}_3$ to the dark antimonial silver ore AgS, SbS_3 . All endeavours, however, as just observed, were unsuccessful. The pentasulphide of antimony in combination with 3 equivalents of disulphide of copper, corresponding to *Guayacanite* (the new mineral I described in the paper above referred to) which consists of pentasulphide of arsenic, with 3 equivalents of disulphide of copper, is also unknown at present.

Further investigations, however, led to the discovery of many singular specimens, some of which, though not altogether new to mineralogical science, may prove interesting to the Society.

Protoxide of Copper.—The combination of one equivalent of copper with one of oxygen, as a mineral production, is rather rare. The suboxide of copper so frequently encountered where the native metal prevails, appears, upon exposure to the atmosphere, or from other causes more difficult to explain to pass at once to the dicarbonate, assuming at the same time both oxygen and carbonic acid. The black earthy looking belt, which so frequently surrounds masses of ruby copper, and which is described in some works as the protoxide, contains, as far as my own experience extends, a very large proportion of sulphur, and although, not perhaps, a true definite oxysulphide, can by no means be regarded as a protoxide; in fact it contains no protoxide whatever, but is a mixture of disulphide and suboxide of copper. The black oxide of copper had only been known as existing in the Vesuvian lavas, until the great discoveries in North America, both in the valley of the Mississippi and on the borders of lake Superior, revealed this mineral in comparatively large quantities. Quite recently extensive veins of copper ore have been discovered in the extreme north of Chile (at longitude 25° S.), consisting essentially of protoxide of copper associated with carbonate of lime and a dark lustrous mineral, apparently a variety of hornblende. The ore, which has a dark brown earthy aspect, effervesces strongly upon addition of hydrochloric acid, so that at first it might be supposed to be a combination of the metal with carbonic acid; but that this is not the case is evident, upon a closer investigation of

the mineral, as well as from the fact that it can be ignited to low redness, and maintained at that temperature for some little time, without suffering much diminution in weight, whereas the carbonates of copper are deprived of their carbonic acid almost instantaneously when exposed to high degrees of heat. A qualitative examination showed the presence of oxide of copper, sesquioxide of iron, carbonic acid, lime, chlorine, water, and a substance insoluble in acids. A quantitative analysis gave the following numbers :—

Copper	36.34
Lime	11.61
Peroxide of iron . .	7.87
Carbonic acid . .	9.32
Chlorine	0.25
Water	0.28
Residue	25.23
	<hr/>
	90.90

The chlorine in the mineral was associated with copper, oxide of copper, and water, forming the oxychloride of the metal, and the carbonic acid with the lime, as 11.61 of that earth requires 9.12 of carbonic acid to form a carbonate, and analysis shews 9.32. The greater part of the copper evidently exists as protoxide, and the constitution of the mineral may be thus expressed:—

Oxide of copper	42.92
Oxychloride of copper (3CuO , CuCl , 4HO) . .	2.89
Carbonate of lime	20.73
Peroxide of iron	7.87
Residue	25.23
Loss	0.36
	<hr/>
	100.00

If the impurities be removed, viz., the residue insoluble in acids, peroxide of iron and carbonate of lime, we obtain

Oxide of copper	93.69
Oxychloride of copper . .	6.31
	<hr/>
	100.00

Black Amorphous Sulphate of Lead.—An exceedingly curious form of sulphate of lead was found in a mine a few leagues N.W. of Coquimbo. It occurred in large black masses, in the centre of which a small vein of finely grained galena was running. The sulphate, having a black earthy appearance, with no trace of metallic lustre was rejected by the miners as worthless. Its high specific gravity proved however that it consisted essentially of a compound of one of the heavier metals, and analysis shewed that it was sulphate of lead coloured with a small percentage of protoxide of iron. Hydrochloric acid at the boiling temperature decomposed it entirely, forming a pale green solution, due to protochloride of iron, or rather perhaps protosulphate, as free sulphuric acid existed in the liquid, and on cooling the greater part of the lead was deposited as chloride. Sp. gr. of the mineral 6.20 100 grs. yielded

Sulphate of lead . . .	96.74
Protoxide of iron . . .	3.16
Silver	traces
	<hr/>
	99.90

The galena, which formed as it were the nucleus of the mass contained (as is generally the case with the fine-grained sulphide of lead) appreciable quantities of silver, far more so than the exterior sulphate.

Basic Persulphate of Iron.—This beautiful mineral has been described in mineralogical treatises as *fibroferrite*. As however numerous sulphates appear to exist, among which may be mentioned, Fe_2O_3 , SO_3 , generally cited in chemical works as the one found native in South America, an account of the true fibroferrite may not perhaps be out of place.

This mineral is found in botryoidal masses, each rounded nodule being built up of innumerable silky fibres diverging from the centre, and of a pale golden green colour. It consists of two equivalents of sulphuric acid in combination with one of sesquioxide of iron (Fe_2O_3 , 2SO_3), and 10 of water.

	Calculated.	Found.
Sulphuric acid . . .	32.0	31.94
Peroxide of iron . . .	32.0	31.89
Water	36.0	35.90
	<hr/>	<hr/>
	100.0	99.73

After exposure to the air for a few weeks, it loses two equivalents of water and becomes $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 8\text{HO}$, and does not decrease further in weight even after many months. Heated in a water bath at 212°F ., it loses 7 atoms of water, the residue consisting of $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 3\text{HO}$, and it requires a very high temperature for the expulsion of the last 3 equivalents. When subjected to a temperature of between 500° to 600°F . for some hours, the whole of the water is expelled and a pure bisulphate of peroxide of iron, perfectly anhydrous, remains.

	Calculated.	Found.
Peroxide of iron .	50.00	49.87
Sulphuric acid .	50.00	49.98
	<hr/> 100.00	<hr/> 99.85

When fibroferrite is digested in cold water, it is partially dissolved, the solution containing both iron and sulphuric acid, and having a slightly acid reaction to test paper. The phenomena produced by the action of boiling water are interesting. The mineral becomes decomposed at a temperature of about 120°F ., into an ochreish yellow amorphous substance, and a soluble salt, the solution of which is strongly acid. 10.00 grains of fibroferrite were digested in boiling water for an hour, and the residue dried on a water bath at 212° . This insoluble portion weighed exactly 3.00 grains, and yielded on analysis 2.100 peroxide of iron, .528 sulphuric acid, and .368 water, being evidently a combination of 2 equivalents of peroxide of iron, with 1 of sulphuric acid, and 3 of water.

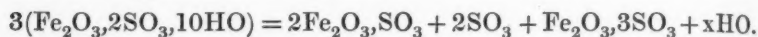
	Calculated.	Found.
2 Fe_2O_3 . . .	70.49	70.00
1 SO_3 . . .	17.61	17.60
3 HO . . .	11.90	12.26
	<hr/> 100.00	<hr/> 99.86

or $2\text{Fe}_2\text{O}_3, \text{SO}_3, 3\text{HO}$.

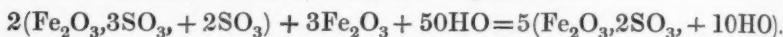
The sulphuric acid in the filtrate was found to weigh 2.640, and the peroxide of iron 1.06, the loss agreeing very closely with the 7 equivalents of water which separated at 212° .

Sulphuric acid evidently exists in a free state, as well as in combination with peroxide of iron, as the persulphate. Thus it

appears that 3 equivalents of fibroferrite have split up into 1 equivalent of a very basic sulphate, 1 of ordinary sesquisulphate, 2 of free sulphuric acid and water.



The insoluble compound described above is found native, and very often associated with fibroferrite. Should the sesquisulphate of iron and free sulphuric acid come in contact with sesquioxide of iron and water, fibroferrite might be reproduced.



It is somewhat singular that from $\text{Fe}_2\text{O}_3, 2\text{SO}_3$, in which two atoms of acid are united with one of base, a compound with two of base with one of acid should be derived.

Bournonite.—Bournonite was unknown in South America, and I believe in the New World, until the year 1858, when I met with it in a mine near Huasco, in the northern part of Chile. The specimen was crystallized. Hardness 2·5; specific gravity 5·80. It resembled in every respect the samples found in Cornwall and some parts of Germany. 100 grains yielded—

Sulphur	20·45
Antimony	26·21
Lead	40·76
Copper	12·52
						<hr/>
						99·94

A specimen from Cornwall gave—

Sulphur	20·30
Antimony	26·30
Lead	40·80
Copper	12·70
						<hr/>
						100·10

This mineral is mentioned in the present memoir not only as being the first of the kind found in America, but also for the purpose of introducing a few remarks, relative to the separation of arsenic and antimony, from lead, copper, and other metals of that group. In 1854 MM. Rivot, Beudant, and Daguin, published a very interesting paper in the *Comptes Rendus*, wherein it was pro-

posed to separate antimony, arsenic, and sulphur from many other elements, by digesting the mineral in a warm solution of potash, which after a time dissolved the arsenical and antimonial sulphides, and passing a stream of chlorine through the potash solution, by which were formed sulphuric, arsenic, and antimonious acid. By adopting this means, the authors remark, the whole of the antimony, arsenic, and sulphur, may be removed from lead, copper, &c. I have repeatedly tried this process, and although in my experiments, the minerals were in a very finely divided condition, complete decomposition, especially when antimony was present, could not be effected. In most instances, much of that element and nearly all the arsenic were dissolved, but even after many days digestion, antimony was invariably found in the residue. Hypochlorites of the alkalies or alkaline earths do not answer better. Dr. Aug. Streng (Ann. Ch. Pharm., xcii, 411, and Chem. Gaz., xii, p. 269), endeavoured in his volumetrical determination of lead, to decompose galena with hypochlorite of lime, but without success. I also have tried hypochlorite of soda upon that and many other minerals with equally unsuccessful results. Streng, however, acted upon the galena with strong nitric acid, thus converting it into sulphate of lead, and then, after neutralizing the fluid with potash, digested, at a temperature a little below 212°F ., with chloride of lime, when after some time, decomposition was complete, the whole of the sulphate of lead having passed into the state of peroxide. When bournonite is treated in the same way, chloride of soda being employed, instead of the lime-salt, a considerable quantity of antimony passes into solution, but 2 or 3 per cent. always remains in the residue.

The process answers admirably in the analysis of copper or lead minerals containing arsenic and sulphur. For *guayacanite*, ($3\text{Cu}_2\text{S}, \text{AsS}_3$) for example, the mineral is finely pulverized, digested in fuming nitric acid, and evaporated nearly to dryness; hypochlorite of soda is then added in considerable excess, and the whole boiled for about 20 minutes. All the arsenic and sulphur pass into the filtrate, pure oxide of copper remaining undissolved.

The same is the case with the sulpho-arsenides of cobalt and nickel. The stronger solutions of potash and soda in very great excess, and after violent ebullition, fail to decompose the arseniates of these metals completely; but if a stream of chlorine be passed through the alkaline liquid previous to boiling, or which is simpler,

a hypochlorite be at one employed, no trace of arsenic can be detected in the residual oxides.

Double Sulphide of Copper and Lead.—This very rare mineral, which I discovered in a mine near the silver district of Arqueros, consists of three equivalents of disulphide of copper and one of sulphide of lead, differing entirely from *Cuproplumbite* Cu_2S , 2PbS , also from Chile, which was analysed by Plattner, many years ago. 100 grs. of the new double sulphide yielded—

Copper	53.28
Sulphur	17.69
Lead	28.81
						99.78

or $3\text{Cu}_2\text{S}, \text{PbS}$

		Calculated.	Found.
3Cu_2	.	53.34	53.28
4S	.	17.78	17.69
1Pb	.	28.88	28.81
		100.00	99.78

It may be mentioned that this mineral has received the name *Alisonite*, in honour of Mr. Robert E. Alison, a gentleman who from his extensive smelting operations in no less than five different points in the Republic of Chile, has effected very much in the development of the mineral riches of South America. I observe that the great American Minerologist Dana, to whom I sent a short note upon the mineral in question, has published it under the name *Alisonite* in his supplement to the last edition of his work.

This mineral adds another to the list of the tribasic sulphides which have been already discussed in the two papers I have had the honour of transmitting to the Society.

Arsenical Rosicler	$3\text{AgS}, \text{AsS}_3$
Antimonial do	$3\text{AgS}, \text{SbS}_3$
Sulphide of copper and arsenic	$3\text{Cu}_2\text{S}, \text{AsS}_3$
Guayacanite	$3\text{Cu}_2\text{S}, \text{AsS}_5$
Alisonite	$3\text{Cu}_2\text{S}, \text{PbS}$

Mr. David Forbes, on his return from Chile, published an

account of a new arsenide of copper in the Philosophical Magazine for last December, and has named it *Darwinite*. This adds another to the list of arsenides, the first of which is *Domeykite*, and the second *Algodonite*, of which I published an account in the Journal of this Society in 1857.

Domeykite	Cu_6As
Algodonite	Cu_{12}As
Darwinite	Cu_{18}As

XIV.—On the action of Dibromide of Ethylene on Pyridine.

By JOHN DAVIDSON.

RECENT researches have proved that the bromides of the diatomic radicals are capable of fixing either one or two molecules of ammonia and the monamines, the bromides of a monamonium and of a diammonium being thus produced.

This fact having been hitherto almost exclusively established by experiments with the ethylated bases of the nitrogen and of the phosphorus-series, it appeared desirable, for the sake of generalization, to extend these observations to the several other groups of monamines.

Among the numerous bases which presented themselves for an examination of this kind, the group of basic compounds isomeric with the aromatic bases could not fail to attract my attention. Pyridine, picoline, &c., discovered by Dr. Anderson, are powerful monamines, the tertiary character of which is well established by their deportment with iodide of ethyl; the advanced degree of substitution rendered these substances particularly well adapted for the intended experiments.

Pyridine, as is well known, has been obtained in the destructive distillation of coal, of certain varieties of shale, and of animal substances. The substance* which I had at my disposal was

* I am indebted to Mr. Samuel Clift, of Manchester, for a considerable supply of pyridine and all the other bases formed in the destructive distillation of coal.—A.W.H.

procured from coal tar. It was separated from the picoline by distillation; the specimen with which I worked boiled constantly at 118°·5 C.

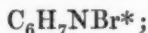
A mixture of pyridine and dibromide of ethylene gradually darkens and ultimately becomes brown; no crystals, however, are deposited. On the other hand, the reaction proceeds with great rapidity at 100° C.; and if this temperature be continued for about three hours, an almost black and crystalline mass is formed, from which by successive treatment with cold, and crystallisations from boiling alcohol, a beautiful bromide crystallising in silky plates may be eliminated. In preparing this bromide, it is advisable to add to the mixture of the anhydrous substances, from one-fifth to one-sixth of its volume of alcohol and to digest at 100°C. in sealed tubes; in this manner, the whole liquid solidifies into a silky crystalline mass, which, being but very slightly coloured, is much more easily purified. The new bromide may also be prepared by digesting at 100°C. a mixture of pyridine and dibromide of ethylene with an equal bulk of alcohol, in a flask provided with a condensing tube. This process, however, is less expeditious, and is apt to occasion a loss of pyridine, which may be carried off with the alcohol-vapour.

The crystalline bromide, although not deliquescent, is very soluble in water; I did not succeed in getting crystals from the aqueous solution; it is exceedingly soluble in boiling, and only slightly so in cold alcohol. The boiling alcoholic solution solidifies on cooling into a pearly crystalline mass; dilute solutions on cooling, or on spontaneous evaporation, yield larger plates, which are transparent, but were never sufficiently well formed for determination.

I. When burned with chromate of lead, 0·206 grm. of the bromide previously well dried at 100°C., gave 0·316 grm. of carbonic acid and 0·077 grm. of water.

II. 0·4165 grm. of the bromide, when precipitated by nitrate of silver, gave 0·452 grm. of bromide of silver.

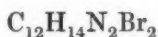
The simplest expression representing these numbers is



but the mode of formation of the new compound shows unmistakably that this expression must be doubled, and that the compo-

* H = 1; O = 16; C = 12 &c.

sition and weight of the molecule of this compound is represented by the formula,

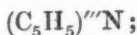


Theory.			Experiment.	
			I.	II.
C_{12}	= 144	41.62	41.69	„
H_{14}	= 14	4.04	4.15	„
N_2	= 28	8.10	„	„
Br_2	= 160	46.24	„	46.16
	<hr/>	<hr/>		
	346	100.00		

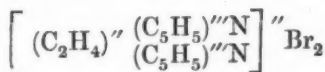
Pyridine, therefore, imitates triethylamine and triethylphosphine in its deportment with dibromide of ethylene, the new bromide being formed by the union of one molecule of the latter with two molecules of pyridine:



The constitution of pyridine itself is but imperfectly made out. All that we know is that this substance is a tertiary monamine; the nature of the radicles which replace the hydrogen is as yet unknown. In accordance with our present knowledge, pyridine is represented by the expression

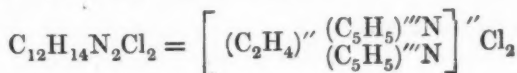


whence the molecular construction of the new bromide may be expressed by the formula



The composition of the dibromide is confirmed by the analysis of the chloride and of platinum-salt.

Dichloride.—Treatment of the dibromide with chloride of silver, yields, on evaporation of the liquid obtained, the corresponding dichloride, which is a white crystalline exceedingly soluble and deliquescent substance. 0.232 grm. of the dichloride, dried at 100°C , and cooled *in vacuo*, gave 0.259 grm. of chloride of silver, showing 27.62 per cent. of chlorine, which is exactly the percentage required by the formula



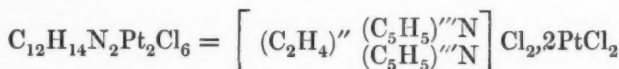
Platinum-salt.—The solution of the dichloride yields, with dichloride of platinum, a pale yellow and apparently amorphous precipitate, insoluble in water or alcohol, but slightly soluble in boiling concentrated hydrochloric acid, from which on cooling it is almost entirely deposited again in the form of little brilliant yellow plates.

I. On burning the platinum-salt with chromate of lead, the following results were obtained :

0.415 grm. of substance gave 0.36 of carbonic acid and 0.1006 of water.

II. 0.312 grm. of the platinum-salt on ignition gave 0.1032 grms. of metallic platinum.

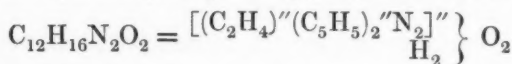
The formula



requires the following values :

Theory.			Experiment.	
			I.	II.
C_{12}	= 144	24.120	23.63	„
H_{14}	= 14	2.345	2.67	„
N_2	= 28	4.690	„	„
Pt_2	= 198	33.167	„	33.3
Cl_6	= 213	55.678	„	„
		<hr/>		
		597	100.00	

The solution of the dibromide, when mixed with freshly precipitated oxide of silver in the cold, furnishes a transparent, colourless, and powerfully alkaline liquid, which contains the corresponding base, viz : the *hydrate of ethylene-dipyridyl-diammonium*.



The existence of this compound in the solution is readily proved by saturating the caustic liquid with hydrochloric acid, and adding dichloride of platinum, whereupon the pale yellow salt previously mentioned is immediately precipitated. It was identified by analysis.

0.185 grm. of platinum-salt left, on burning, 0.0612 grm. of metallic platinum corresponding to 33.08 per cent., the theory requiring 33.16 per cent.

The hydrates of the diatomic pyridyl-derivatives are how-

ever far less stable than the ethylated diatomic bases in the nitrogen- and phosphorus-series. Even at the common temperature, and more rapidly so on heating the solution of the free base becomes pink, violet, and ultimately ruby-red, and deposits after some time a brown powder, a peculiar odour resembling that of heliotrope being evolved at the same time. I have not examined more minutely the changes which the pyridine-compound thus undergoes. I will only mention that the solution, when it had become coloured, no longer yielded the difficultly soluble precipitate with dichloride of platinum, a crystalline platinum-salt being deposited only after a considerable time; on the other hand, when boiled for some minutes, and separated from the brown compound which is deposited, the liquid again gave a yellow amorphous platinum-salt.

I have made also a few experiments with picoline, homologous to pyridine and isomeric with phenylamine. This base is likewise acted upon by dibromide of ethylene, but far less energetically than pyridine: digestion for four hours at 100°C. produced but a slight change; after digestion for several hours at about 150°C. the mixture was black, but had not deposited any crystalline matter; after several days, crystals began slowly to form. I have not examined this reaction any further.

The above experiments were performed in Dr. Hofmann's laboratory.

XV.—*Account of recent researches on the application of Electricity, from different sources, to the explosion of Gunpowder.*

By F. A. ABEL, F.R.S., Director of the Chemical Establishment of the War Department.

THE employment of electricity as an agent for affecting the ignition of gunpowder, suggested itself to Franklin,* in 1751, and to Priestley, in 1767 but it was not until some years after the

* In his "Letters on Electricity," dated 29th June, 1751, Franklin says, "I have not heard that anybody in Europe has yet succeeded in firing gunpowder by means of electricity. We do it in this way: a small cartridge is filled with dry powder, which is rammed in tightly enough to crush a few grains; two pointed brass wires are then fixed in it, one at each end so that their points are not further apart than half an inch at the centre of the cartridge, which is then placed in the circuit of the electric machine; when the communication is completed, the flame, leaping from the points of one wire to that of the other, through the powder in the cartridge, fires it instantaneously."

discovery of the electric pile by Volta, that earnest endeavours were made to apply electricity to military and mining purposes. In 1832, the first experiments on the application of voltaic electricity in this direction appears to have been made by French Military Engineers; about twelve years afterwards, that agent was first successfully employed in important blasting operations (such as, in England, the destruction of the Round Down Cliff, near Dover, and of the wreck of the Royal George, at Spithead), and from that period until very recently, the applications of electricity to mining purposes have been almost entirely confined to the employment of the voltaic current.

The methods which have been most generally used, up to the present time, for the explosion of gunpowder by the direct agency of voltaic batteries of different kinds, are so well known to all who have given their attention to experimental electricity, that a brief statement of the principles upon which they are based, will suffice. The original method, and that still principally used in military operations, when the voltaic battery alone is employed, consists in causing the current (at the place where the powder is to be exploded), to traverse a short piece of fine wire, made of some metal of inferior conducting power, such as platinum or iron, which, in consequence of the resistance offered by it to the passage of the current, is raised to a red heat on completion of the metallic circuit, of which it forms a portion. The thin wire is surrounded with fine-grain gunpowder, and is generally fitted into some simple arrangement, which may readily be connected with the circuit-wires, and brought into close contact with the charge to be exploded.

The other approved method of affecting the ignition of a charge of powder by a voltaic current, consists in the employment of an ingenious contrivance, first introduced by Messrs. Statham and Brunton, and founded upon an observation made in experiments with a submarine telegraph-wire, which had been insulated with gutta-percha impregnated with sulphur. Some amount of chemical action is exerted between the sulphur and the copper, in covered wire of this description, in consequence of which, the surface of gutta-percha in contact with the wire becomes coated with particles of subsulphide of copper, which remain attached to it on the removal of the wire. This coating of subsulphide is a sufficiently good conductor of electricity to assist the passage of a current of low tension across a small interruption in the metallic circuit; the

heat resulting from the retardation of the current at such a point is, however, sufficiently intense to effect the ignition of some very combustible substance. It is obvious that this fact admits of ready application to the construction of an arrangement for the ignition of gunpowder, in which contrivance a hollow piece of gutta-percha, coated on the interior with the sub-sulphide of copper, is made to replace the fine platinum- or iron-wire above referred to. The Statham fuze, constructed upon this principle, has been found under favourable conditions, which have been fully discussed in other memoirs relating to this subject, to present important advantages over the method of igniting gunpowder by means of fine wires.

Although the employment of voltaic currents for the ignition of charges of gunpowder obviously presents great advantages over the old system of firing mines or cannon (by means of slow and regular-burning matches or fuzes, the length and time of burning of which was proportioned to the interval which it was desired should elapse between their first ignition and the explosion of the charge), its application, especially to military purposes, is attended with an amount of uncertainty which has precluded it from ever acquiring great confidence on the part of engineering authorities. This uncertainty is, it need scarcely be said, due mainly to the great difficulty of ensuring a sufficient uniformity of action at different periods of time, even with the most efficient voltaic arrangements, and of securing the safe transport and proper preservation of any battery-arrangement, and of the agents necessary for its application. When it is remembered that, besides these difficulties, there are others not less serious, which result from the uncertainty of ensuring proper attention to the numerous little points, of vital importance to success, connected with such an application of electricity of low tension, it will be readily conceived that, almost ever since the first practical application of electricity to the ignition of charges of powder, the possibility of rendering electricity of high tension available in this direction, and of applying to military operations the valuable discoveries of Faraday in electro-magnetism, has received from time to time, serious attention on the part of military engineers and others specially interested in operations of this kind.

Thus, experiments furnishing interesting and important results have been instituted on the application of induced currents, and of

frictional electricity to the explosion of gunpowder, in Spain, France, Austria, Russia, and other countries; and, in 1855, Professor Wheatstone suggested to General Sir John Burgoyne the institution of an experimental enquiry in this country into the relative advantages offered by electricity of high tension, obtained from different sources, as applied to the explosion of gunpowder. In consequence of this suggestion, a long series of experiments has been carried out by Professor Wheatstone and myself, by desire of the Secretary of State for War, and, at first, in connection with the Ordnance Select Committee. The most interesting and important of the results arrived at by those investigations will form the principal subjects of this memoir.

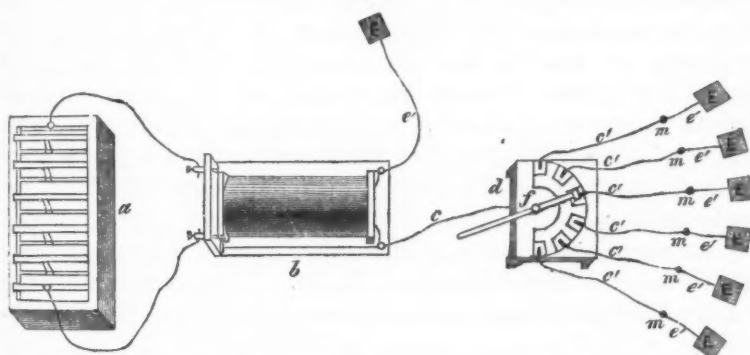
Although our experiments with volta-induction apparatus, with frictional electricity, and with the currents induced by permanent magnets, were conducted, in great measure, at the same time, it will be advisable to avoid confusion by giving, under separate heads, on account of the results furnished with each form of electricity, and of the conclusions deduced from them.

I.—EXPERIMENTS WITH ELECTRO-MAGNETIC INDUCTION APPARATUS.

The first application, with practical success, of the form of electricity furnished by volta-induction apparatus to military purposes was made in 1853 by a Spanish officer, Colonel Verdu, who, having witnessed the firing of a gun at Dover by the agency of a voltaic battery at Calais, connected with the gun by means of a submarine cable, was much struck with the inconvenience resulting from the necessity of employing very great battery-power for effecting the discharge of gunpowder at considerable distance, it having been necessary on this occasion to use a battery of 400 of Bunsen's cells. The first investigations of Colonel Verdu were made with the assistance of M. Ruhmkorff, and with the induction coil-machine which had been recently perfected by the latter. The success attending the first experiments led to further trials in Spain, where Colonel Verdu succeeded, with the employment of only one element of Bunsen's battery, in exploding simultaneously six mines in one circuit, at a distance of 300 metres. This result was, of course, obtained by allowing the current to leap across small interruptions in the metallic circuits, which were surrounded with a readily inflammable substance, and imbedded in the charges of powder. The fuze employed was, in fact, that of Statham, in

which the terminals were surrounded by fulminate of mercury. Still greater results were obtained by arranging the mines in groups of five, so that each group formed a special circuit; by then bringing each circuit, in very quick succession, in connection with the instrument, the mines were all discharged with a rapidity which had the practical effect of a simultaneous discharge. The reason why Colonel Verdu resorted to this method of operation is, that the discharge from an induction coil-machine, unlike that from a Leyden jar, which will pass through several hundred solutions of continuity, producing a spark at each interruption, becomes so enfeebled by successive interruptions in the metallic circuit, that it is impracticable to ignite, with certainty, a number of charges in one circuit, beyond certain limits, which, with the fuzes used by Colonel Verdu, were very narrow.

Fig. 1.

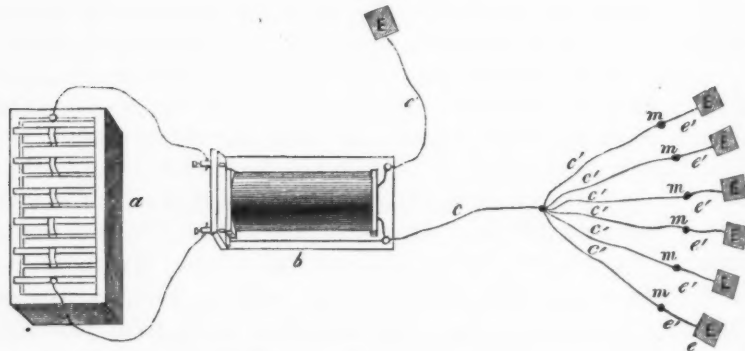


The arrangement of charges, &c., upon this system is exhibited in Fig. 1, in which *a* and *b* represent the battery and coil-machine; *c*, the wire connecting one pole of the latter with an instrument, *d*, called a *rheotome*, provided with binding screws for receiving the separate wires *c'*, which lead to the mines *m*. These screws are fixed into small copper plates isolated from each other, being either let into the wood, or separated by strips of glass. The wire *c* from the coil-machine is in connection with a species of metal finger, *f*, which, by means of an insulating handle, may be made to describe a semicircle with optional rapidity; and, as its one extremity presses firmly upon the instrument at a point near any one of the binding screws, it is brought alternately into contact with the several small metal plates with which they are connected, thus bringing them (and therefore the mines) into connec-

tion with the coil-machine. This is only one of several contrivances which have been used for producing successive discharges of mines upon this principle. In the above arrangement, the wires e' and the plates of metal E connect the charges and coil-machine with the earth.

A method of securing the practically simultaneous discharge of a number of mines, more effective than the so-called *rheotomic* arrangement of Colonel Verdu, was afterwards devised by M. Savare, who appears to have first conceived the idea of dividing the circuit into branches, over the whole of which a current, or rapid succession of currents, are distributed, on the completion of the circuit, with an uniformity regulated by the degree of resistance met with in each branch. Thus, on interposing one or more fuzes in each branch of the circuit, those which happen to offer greater facilities, in their construction, to the passage of the current, would explode first, and, the fuzes being so constructed that the terminals of the wires in them are forced apart by the explosion or fused by the heat generated, the further passage of the current in that direction is prevented, and the remaining fuzes are in their turn exploded. It is readily conceivable that, with the employment of currents of high tension, following each other with the enormous rapidity with which they pass off from the coil-machines, the discharge of a number of fuzes may be effected by the above arrangement with a rapidity which has practically the effect of a simultaneous discharge. Experiments with this mode of discharge were made at Grenelle in 1854. The arrange-

Fig. 2.



ment of charges, discharging instrument, connections, &c., is illustrated by Fig. 2, which scarcely needs special explanation (the

letters of reference used corresponding in their meaning to those in Fig. 1, and the principal difference being that the branch-wires are connected directly with the wire leading to the machine, instead of by the agency of a rheotome.)

The Ruhmkorff's coil appears, without doubt, to have been used by the Russians in their mining operations at Sebastopol. But the most extensive application hitherto made of that instrument for the explosion of mines has been in the great operations undertaken by Messrs. Dussaut and Rabatt u at the Port of Cherbourg, in 1854, according to a system organized by the Vicomte du Moncel, and which was a modification of Colonel Verdu's method. At the first trial, six mines, containing each about 4,400 kilos. of powder, were inflamed as with one detonation, detaching at once more than 50,000 cubic metres of rock.

When the experiments at Woolwich were first undertaken in 1856, much uncertainty appeared still to prevail regarding the description of priming materials best adapted for employment in fuzes to be used with the volta-induction current, and the maximum number of charges which could be fired *with certainty* by means of a powerful coil-machine and a battery of moderate power. Experiments were therefore undertaken to obtain information on these points, and to ascertain the extent to which an electro-magnetic coil, of the best and most portable construction, would be likely to resist injury by ordinarily careful use and by transport.

The coil-machine used in the first experiments was one of considerable size and recent construction, prepared by M. Ruhmkorff. Another apparatus, of similar power, but constructed for the Ordnance Select Committee by M. Ruhmkorff, with especial regard to its service in the field, was also subsequently employed in many of the experiments. A battery of cast-iron cells and zinc plates (the dimensions of the latter being 5 in. by 3 in.) was employed, as the most economical for general purposes.

In the greater number of the experiments, the current was made to pass to the charges or fuzes through one mile of copper wire (16 gauge), insulated with gutta-percha, the metallic circuit being, in many instances, interrupted by an earth-connection of about 200 yards in length.

The results furnished by a large number of experiments were briefly as follows:—

Fine-grain or mealed gunpowder was found to be ignited readily, by means of the induction-coil, with the employment of one

cell of the battery. Numerous substances of a more highly explosive character were tried, alone, and in admixture with gunpowder, in order to arrive at the description of priming material most suitable to aid in effecting the ignition of the maximum number of charges by means of the coil-machine. The best results were obtained with fulminate of mercury. The efficacy and delicacy of the fuze were also found to depend in very great measure upon a proper adjustment of the wire-terminals which it enclosed.

The number of charges placed in succession, in single circuit, which could be fired at one time by means of such coil-machines as those used, and with the employment of twelve cells of the battery specified above, did not exceed eight (and was generally below that number) even when priming compositions of a sensitive character, containing fulminate of mercury, gun-cotton, sulphide of antimony and chlorate of potassa, &c., were employed. The discharge of this number could not, however, be relied upon with any certainty; and the employment of twelve cells did not appear to offer any decided advantage over the use of only four. The ignition of two charges could be effected almost with certainty by the employment of only one cell, and the result appeared to be rendered certain by the use of four cells.

By employing a rheotomic arrangement for changing the direction of the current, so as to bring wires connected with one or more charges successively into the circuit (as described just now), a considerable number of charges could be fired in very rapid succession. This result was, however, perfectly certain only when a single charge was brought into the circuit at one time.

Upon employing M. Savare's arrangement of branch-circuits, so as to allow the current, when established, to distribute itself along each divided portion of the circuit, and ignite simultaneously, or in rapid succession, the several fuzes which were introduced, five or six charges were exploded at one time, and a far more considerable number ignited, with a rapidity almost instantaneous; as, when this arrangement is employed, the first of the very rapid succession of currents established by the coil-machine passes through and ignites those fuzes which offer the least resistance, while the others are fired in their turn by the succeeding currents. This method of exploding a number of charges at once, or in very rapid succession, is undoubtedly more efficient than the best rheotomic arrangement, and it renders the operator independent

of the uncertainty of firing three or four charges simultaneously, when arranged in a simple circuit; for, in the latter case, if the ignition of the whole number is not perfectly instantaneous, the explosion of the first prevents the discharge of the remainder; while, in the arrangement just referred to, the connection of each fuze with the instrument is independent.

In the course of these experiments carried on with the two coil-machines constructed by M. Ruhmkorff (one of which was, as already stated, specially prepared for operations in the field), a considerable irregularity was observed in the power of the same machine at different periods, although the battery-power employed was, to all appearances, the same on each occasion,—an irregularity which must be ascribed to defective insulation, arising from the deposition of moisture on some portion of the apparatus. It was found that the arrangement attached to the coil-machine, known as the condenser, and upon which the intensity of the current produced greatly depends, was very liable to be put out of order in the transport of the apparatus, and by other trifling causes; any derangement of this part of the apparatus was fatal to its efficiency. The perfect insulation of each coil of the secondary wire and other somewhat delicate portions of the apparatus, were also found liable to injury from a variety of sources, which it would be very difficult to guard against in the employment of coil-machines for field purposes, and by persons not thoroughly acquainted with their somewhat complicated construction and their action.

Although, therefore, the system of exploding charges by means of the induction coil-machines, offers several very important advantages over the voltaic battery, employed alone (one of the principal being the great reduction effected by its use in the power of battery required) its adoption as a general substitute for the old system of operation with the battery cannot be recommended with confidence, principally because proper reliance cannot be placed upon the certainty and permanent uniformity of action of the apparatus.

Some experiments which I have instituted quite recently, combining the use of one of the coil-machines above referred to, with that of the new description of fuze devised by me for employment with magneto-electric apparatus (to be presently described), furnished results greatly surpassing in magnitude and certainty any which have hitherto been obtained with volta-induction currents.

Employing only six cells of a small Smee's battery, from ten to fifteen charges were fired with certainty when arranged in a simple circuit; fifty charges (arranged in branch circuits, in sets of ten) were ignited with the effect of one explosion, and there is no doubt that this result might be considerably exceeded with the introduction of a larger number of branches into the circuit arrangement.

It must be borne in mind that these results were obtained with a coil-machine made by Ruhmkorff in 1855. The very important improvements which have recently been effected by Ladd, Bentley, Ruhmkorff, and others in the construction of the induction coil-apparatus, have reduced to comparative insignificance the most powerful results furnished by the Ruhmkorff coil, as constructed five or six years ago. There is no doubt that, with the combined employment of the new fuzes and of one of the larger induction coil-machines of recent construction, the simultaneous ignition of several hundred charges could be effected without difficulty, and that, in operations of very great magnitude, such an instrument may be employed with confidence as the most efficient agent for effecting the explosion of mines.

II. — EXPERIMENTS WITH FRICTIONAL ELECTRICITY.

It has already been stated that, as early as the middle of the eighteenth century, Franklin and Priestly both directed their attention to the application of electricity from the machine to the ignition of gunpowder; but it was not until 1831 that an actual application of frictional electricity to mining purposes was first made by Moses Shaw, of New York, who, with fuzes charged with gunpowder and fulminate of silver, succeeded in exploding several mines simultaneously, detaching large masses of rock. It is stated by him, in his account of the experiments, that he was unable to operate during the greater part of the year, on account of bad weather. In 1842 and 1843, Messrs. Warrentrap, of Brunswick, and Götzmann, of Freiburg, made more successful experiments. Having effected improvements in the insulation of the conducting wires used, and employing fuzes which contained a mixture of sulphide of antimony and chlorate of potassa, they succeeded in exploding from eight to ten mines simultaneously through 78·5 metres. Notwithstanding these results, they were compelled to abandon the attempt to employ electricity as a certain agent for the explo-

sion of gunpowder, on account of the evil influence of atmospheric moisture. In 1845, the subject was again brought up by Mr. Charles Winter, who succeeded in inflaming powder through a telegraph wire, reaching between Vienna and Hetzendorf, a distance of 4,906 metres.

In 1853, when the first successful results had been obtained in France with the Ruhmkorff coil, the Austrian Government directed the Imperial Engineer Academy to propose a system of exploding charges by electricity, to be employed by the Imperial Engineers.

The somewhat complicated character of the induction coil-machine, and the necessity for the employment of some voltaic battery with it, appear to have been accepted, at the outset, by the Austrian investigators as formidable obstacles to the application of the apparatus in question to military purposes. Attention was therefore again directed to the application of frictional electricity; and, after three years' experiments, a system of operation, involving the employment of an electric machine, was considered to have been sufficiently successful for introduction into the engineer service. The system in question appears to have furnished very important results, and to have been frequently applied to industrial operations.

The electric machine employed is arranged in a very portable form, and consists of two discs of polished glass, twelve inches in diameter and four lines thick, fixed upon one axis, within $1\frac{1}{2}$ inches of each other, and fitted with cushions to which springs are attached. The Leyden jar is cylindrical, fifteen inches high and six in diameter (its area being 276 square inches). It is protected by flannel and fixed in a case of lacquered tin, being screwed on to an iron plate which is connected with the friction-apparatus. The charging is effected by means of a steel point, which projects one inch into the space between the discs, and can be pushed into an arm of the conductor. The latter is inserted into a plate of hard caoutchouc which forms the cover of the Leyden jar, and is connected by chains with its inner surface. The machine is always covered, when in use, by a case, the sides of which are made of thick leather and the top of tin. A small stove is also fixed beneath it, so as to dry the air inside when necessary. The wire employed as conductor is brass, which is raised on insulated posts or covered with gutta-percha; the priming material used in the fuzes was, first fulminate of mercury; a mixture of chlorate

of potassa and sulphide of antimony was afterwards adopted. A large number of experiments were tried with this arrangement, under the various conditions in which it might receive application. The greatest distance at which an inflammation was attempted was four German miles. On several occasions, fifty mines were simultaneously discharged in the same circuit; the fuzes were two klafters (toises) from each other, and the electric machine was 140 klafters from the nearest fuze. In like manner, thirty-six charges were simultaneously exploded in one of the branches of the Danube; these charges were placed six feet under water, and had remained submerged during twenty hours previous to their explosion. Other operations on a large scale, in marble quarries, in the beds of rivers, &c., in which considerable masses of matter were displaced, are given in detail in an interesting report by Baron von Ebner, published in 1855; they place the efficiency of the process beyond doubt. The objections to the system, as pointed out in the report referred to, are that some scientific skill is required in the manipulations; that great care is needed in the preservation of the apparatus, and that the inductive action is sometimes so energetic that explosions are occasionally determined in other mines not intended to be included in the series, and not connected with the machine.

At the suggestion of Mr. Wheatstone, a series of experiments was undertaken for the purpose of ascertaining whether the hydro-electric machine of Sir William Armstrong might not be advantageously substituted for the ordinary electric machine for charging a Leyden jar or battery in the field.

A small portable hydro-electric machine was constructed specially for the enquiry, and placed at the disposal of the experimenters by Sir William Armstrong. It consisted of a small vertical boiler (supported on a sheet iron stand in which a grate was fixed), of two gallons capacity, provided with a safety-valve, by which the pressure of steam could be regulated up to 90lbs. on the inch. The head of the boiler was provided with a cock, to admit of the escape of steam, to which was fixed a horizontal iron pipe, nine inches in length, and of half an inch internal diameter, and fitted with the jet and wooden cylinder which serve for the issue of the steam and the development of the electricity. The iron pipe was surrounded by a small metal box, which, when the apparatus was in use, was partly filled with water, so as to effect a partial condensation of the vapour as it passed through the pipe.

A brass fork, raised to a level with the jet, and capable of adjustment at different distances from it, served the purpose of conducting the electricity from the jet of steam to the Leyden jar or jars, which were placed in a sheet-iron casing, immediately under the steam-jet. The boiler was very well adapted to the rapid generation of steam of considerable pressure. About twenty minutes after a wood fire was kindled, a pressure of 60-70lbs. was obtained, the boiler being one-third full of water.

To avoid the possibility of the water in the boiler *priming* during an operation, in which case the charge of a jar with electricity could not be accomplished, it was indispensable that the boiler should not contain too large a quantity of water (it was found safest to employ it not more than one-half full), and that the water should be free from solid matter in suspension. To ensure the fulfilment of the latter conditions, it was necessary, not only to employ perfectly clear water, but to clean out the boiler after each experiment (if spring or river-water were employed), so as to remove all solid matter deposited by the boiling water. With the employment of rain- or distilled water, this precaution was, of course, rendered unnecessary. The time required to charge with electricity a Leyden jar of about $1\frac{1}{2}$ square feet surface, when the machine was in good working order, was found to be from five to seven seconds. The rapidity with which the jar was charged proved, under favourable conditions, to be proportionate to the pressure of steam employed, the most suitable being from 60-70lbs. per square inch.

The first experiments on the ignition of charges were conducted with the employment of only short lengths (from 12 to 50 feet) of wire, to serve as connections between the jar and the charges. The machine was worked in a locality sheltered from wind and draught. The priming composition employed in the charges was the same as that ultimately adopted in the experiments with the magnet, which will be presently described. Two different plans were available for firing the charges: (1.) by completing the circuit before the jar was charged, and allowing the fuzes to be fired by its spontaneous discharge; (2.) by allowing a definite time (about six or seven seconds) for the charging of the jar, before completing the circuit. The first method would be preferable for the ignition of a very large number of charges in the same circuit, as the employment of the maximum charge attainable would thus be secured. If, however, the ignition of the charges had to be effected at

a given time, it would be necessary to employ the second method.

The results obtained by this apparatus were very variable. On one or two occasions (five seconds being allowed for the charging of the jar), it was found impossible to fire six charges, placed in a simple circuit, simultaneously, with certainty; although, when eight, and afterwards twelve, were connected in a similar manner, seven and eleven were fired, the conditions (as to pressure, &c.) being apparently the same. On another occasion, with a pressure of 70 lbs., and an allowance of seven seconds for the charging of the jar, forty fuzes were placed in circuit, and the whole number discharged. One hundred and twenty were afterwards placed in circuit, and of these, one hundred were instantaneously discharged. Attempts were subsequently made, under apparently the same conditions, to obtain a repetition of these results, but without success. Experiments made to effect the ignition of several charges in circuit, through a considerable length (one mile) of covered wire and an earth-connection, were only very partially successful. At first the greater portion of the wire was left in a coil, for the sake of convenience, and only a short earth-connection (about twenty feet) was employed. Very successful, though not uniform, results were obtained, forty and fifty fuzes (the entire number in circuit) having, in some instances, been ignited, while, in others, a few were left in different parts of the circuit.

Upon uncoiling the wire to the extent of about 600 yards, and causing the circuit to be completed by the earth, these results could not be in any way depended upon, and on no occasion were as many as forty charges fired, the number at times not exceeding five or six.

A few experiments made with small Leyden jars, charged with electricity from the ordinary cylindrical machine, were confirmatory of the comparative uncertainty in firing a large number of charges through an extended metallic circuit of considerable length. Forty charges were fired by means of a Leyden jar, containing sixty square inches of surface, the electricity passing through about twenty feet of wire-circuit; but on employing one mile of wire, with an earth-connection, the ignition of twenty-five charges, though once or twice successful, could not be depended upon.

Attempts were made on two occasions to employ the hydro-electric machine in the field. At Chatham, the machine was

placed in the open air, on rising ground, and 880 yards of covered wire were employed, of which about sixty were extended, an earth-connection of that length being used in place of a second wire. Two Leyden jars, each affording about $1\frac{1}{2}$ square feet of surface, formed the battery. They were enclosed in a stout wooden box, and every precaution was taken to have them dry at the commencement of the experiments. The time to be allowed for the charging of these jars, as determined by previous experiments, made in a sheltered locality, was about ten seconds, with the employment of steam at 70 lbs. pressure. The atmosphere was dry, and a slight breeze blowing on the day of experiment. The machine was so placed that the steam-jet should be as little as possible affected by the wind.

Repeated unsuccessful attempts were made to fire fifty charges in circuit; these were then gradually reduced to twenty, when only five were ignited in different parts of the circuit. It was found impossible to charge the jars to more than a very slight extent. This unfavourable result was ascribed, partly to an interference of the slight wind with the steadiness of the jet of steam, and partly to the difficulty of maintaining the Leyden jars in a suitably dry condition. The machine was removed to a trench of some depth, for the purpose of sheltering the steam-jet from the wind, but with no better result. On a second occasion, the machine was sheltered from the wind, which blew freshly, by being placed under a shed. Forty fuzes were placed in circuit, with 200 yards of covered wire, coiled up, and an earth-connection of about twenty feet. The two Leyden jars were employed, and the whole of the charges were simultaneously ignited. The wire was afterwards uncoiled, and the same number of fuzes were again placed in circuit, but these did not fire. On reducing the number to twenty-five, nineteen were exploded, six being left in different parts of the circuit.

These experiments appear to prove beyond doubt that the details, or rather the auxiliaries, of the hydro-electric apparatus employed, must undergo some considerable modifications before anything like definite results can be obtained with it. Arrangements for securing the preservation of the jars in a sufficiently dry condition, and for screening the jet of steam from the prejudicial influences of the wind or draught, might readily be carried into effect, and would unquestionably contribute greatly towards rendering the apparatus more certain in its action.

The results above noticed were, however, sufficiently definite to indicate that, in mining operations of a very extensive character (the destruction of docks, bridges, &c.), where it is desirable to ignite a very large number of charges simultaneously, and at which, as is most generally the case, full appliances and conveniences are at command for thoroughly fulfilling every condition of success, the hydro-electric machine is susceptible of very effective application, though scarcely with the same degree of confidence as could be placed in the certainty of action of volta-induction apparatus of recent construction. For general use in the field, the hydro-electric machine, even if its appliances are arranged in a much more efficient manner than was the case with the one employed, could certainly not be relied upon with the necessary confidence, principally on account of the difficulty of ensuring, in the field, the fulfilment of those conditions which appear essential to the proper generation of electricity by means of the steam-jet.

III.—EXPERIMENTS ON THE APPLICATION OF PERMANENT MAGNETS TO THE EXPLOSION OF CHARGES AND TO SUBMARINE OPERATIONS.

The ignition of gunpowder by the direct magneto-electric current, though well known to be practicable, has never yet been applied to military or industrial operations, and no satisfactory experiments appear to have been made, before those undertaken at Woolwich, showing its practical applicability to these purposes.

In the first experiments on this application of the magneto-electric current, a very large powerful magneto-electric machine was employed, which had been constructed by Mr. Henley (and had been exhibited by him at the Paris Exhibition in 1855). The principle of this instrument was precisely the same as that of the machine devised by Mr. Wheatstone, for ringing magneto-electric bells. Its armature, instead of being rotated, was suddenly detached from the magnet by means of a lever. It was soon established by a few experiments that, even with this instrument, gunpowder itself could not be ignited with any degree of certainty. Results obtained with Statham's and other fuzes, though superior to those furnished by gunpowder alone, were still far from satisfactory. The first efforts were therefore directed to the discovery of a suitable agent to serve as a perfectly certain

medium (or priming material) for effecting the ignition of charges by means of the magneto-electric machine. For this purpose, a variety of compounds and mixtures of a more or less sensitive character, were prepared for trial with the magnet. The following were the principal tried: mixtures of meal powder with powdered coke, with sulphur, with sulphur and iron filings, with iron filings and carbon, with fulminate of mercury, and with the latter in addition to iron filings and to coke; fulminate of mercury percussion-cap composition, alone, and with coke; detonating composition (sulphide of antimony and chlorate of potassa); the same mixed with iron filings and with coke; gun-cotton alone, and mixed with some of the above; amorphous phosphorus, in admixture with oxidising agents. It will be observed that the nature of the above materials was varied so as to test the sensitiveness of readily ignitable substances, both alone, and when mixed with bodies which would serve as electrical conductors.

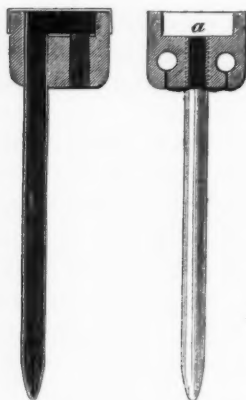
Many of these compositions furnished results to a certain extent favourable, a number of fuzes, primed with them, having been fired in succession with the magnet, and from two to four charges in one circuit having been ignited, in a very few instances. But no perfect certainty of discharge was attained with any one of the above materials; the attempt to fire a fuze being frequently unsuccessful, while no difference between it and a successful fuze, containing the same composition, could be detected by careful examination. These preliminary trials, however, established the fact that the sensitiveness (ready explosiveness) of a priming material was not alone sufficient to determine its success, but that those which possessed a certain, though not too considerable degree, of conducting power, were more readily and certainly ignited than others of a far more sensitive character.

Some successful results, obtained accidentally with one of the experimental compositions, which had become damp by exposure to air, led to a trial of the effect of moisture in promoting the ignition of but slightly sensitive compositions, and it was ultimately found that the impregnation of ordinary gunpowder with a small amount of moisture (by an expedient similar in principle to one adopted with considerable success by Captain Scott, R.E., in connection with charges to be fired by the induction coil-machine), rendered its ignition by means of the magnet a matter of certainty.

Some important precautions were, however, indispensable to

the attainment of this definite result. If the slightly damp powder was employed in a finely divided condition, it very frequently became caked between the wire-terminals in the fuze, and the current would then pass through the composition without igniting it. This was found to take place occasionally, even when the powder was employed in its original granular condition. Several attempts were made to overcome this difficulty by modifying the form and position of the terminals or poles in the fuze, and I at last contrived a perfectly successful arrangement in which only the *sectional surfaces* of the terminals, consisting of fine

Fig. 3.



copper wire (0.022 inch diameter) were exposed in the interior of the fuze (see *a*, fig. 3), so as not to project at all. The prepared gunpowder, therefore, simply rested upon the surfaces, and a perfect uniformity in the action of the fuze was attained. The priming composition consisted of fine-grain gunpowder, which had been soaked in an alcoholic solution of chloride of calcium, of a strength sufficient to impregnate the grains with from one to two per cent. of that salt. The prepared powder was exposed to the air for a short time, to permit of a sufficient absorption of moisture by the deliquescent salt. Upwards of 500 quill-fuzes

(of the description employed for firing guns), primed with the prepared gunpowder, and fitted with the arrangement of the terminals above referred to (fig. 3), were fired with the larger lever-magnet. The failures did not amount to more than 3 per cent., and were all proved to be due to defective manufacture. In the experiments with these fuzes, one or two simple rheotomic arrangements, such as that referred to in the first part of this memoir, were successfully employed for effecting the rapidly successive discharge of a series of fuzes.

The above fuze was found to be easy of manufacture and permanently effective. While, however, it presented a certain means of effecting the ignition by the aid of a powerful magnet, of single charges, or of a large number, to be fired in moderately rapid succession, it was inapplicable to the ignition with certainty of more than one charge in circuit. After a great number of experi-

ments, I at length succeeded in the production of a priming material for the fuze, which greatly exceeded in sensitiveness any of the other compositions hitherto tried. A very gradual separation of the armature from the large magnet sufficed to effect the ignition of the fuzes primed with this material, and the induced current obtained by means of a very small magnet, with a rotatory armature, such as employed in Wheatstone's magneto-electric telegraph, was sufficiently powerful to produce the same result. I have recently found that the currents obtained from magnetic instruments of inferior power and less perfect construction, such as the small American magneto-electric medical apparatus, readily ignite this priming material, and that fuzes primed with it are fired with certainty, by the smallest electro-magnetic apparatus, with the employment of one moderate-sized cell of Smee's battery.

The new priming composition consisted of a very intimate mixture of sub-phosphide of copper, chlorate of potassa, and levigated coke, the latter substance being employed to add to the conducting power of the mixture, which was found otherwise insufficient.

In the course of experiments subsequently carried on with fuzes which contained this composition, it was found that a slight residue, consisting principally of the coke employed, occasionally remained on the surfaces of the terminals in the fuze, after its discharge, and, by forming a good conducting link between them, interfered with any future effects of the magnetic current in other directions, by the establishment of a complete circuit. This obstacle to the perfect success of the composition was entirely removed by the substitution, for the coke, of another material, more easily acted on by the chlorate of potassa, and answering equally well as a conducting medium; namely, the sub-sulphide of copper. No instance has occurred in the discharge of several thousand fuzes, primed with the mixture of sub-phosphide and sub-sulphide of copper with chlorate of potassa, in which the terminals have not been found quite free from adherent residue, after the ignition.

The sub-phosphide of copper, which is produced at an elevated temperature, is a compound of very stable character, and the mixture of the three constituents is quite as unalterable as the explosive mixtures which are in general use for the preparation of percussion caps, &c. The stability of the mixture has already been submitted to very satisfactory tests. Fuzes primed with it

have been found to have lost none of their delicacy and certainty, when tried more than two years after preparation.

Before passing to a statement of the results obtained by the aid of this priming composition, in investigating the extent to which magneto-electricity could be applied with certainty to the simultaneous ignition of a number of fuzes, some little account must be given of the properties of the priming material itself and of the results which regulated the proportions in which its ingredients were employed.

The sub-phosphide of copper, intimately blended with chlorate of potassa, forms a mixture in a high degree sensitive to the effect of heat, and possessed, at the same time, of some power of conducting electricity. With the employment, however, of magneto-electric machines of comparatively low power, and in cases where the resistance to be overcome by the current is considerable, this conducting property is not sufficient to ensure the ignition of the mixture by assisting the passage of the current across the interruption in the metallic circuit (*i.e.*, across the small distance between the terminals of the wires in the fuze.) It must be borne in mind that the striking distance, or the space between the terminals across which the current from even a powerful magneto-electric machine will leap, is very small. With the large lever-magnet, the spark could only be produced when the wires were almost in contact. Since, however, it is indispensable to the proper insulation of the wires in the fuze-arrangement, that the terminals should be at least one-sixteenth of an inch apart, it will be readily understood how essential to success, in operations with these machines, it is that the priming material should possess considerable conducting power. Hence the necessity of increasing the conducting power of the mixture of sub-phosphide of copper and chlorate of potassa; a result which, it has been already stated, was obtained in the first instance by the employment of finely levigated coke, and afterwards, by the substitution of sub-sulphide of copper for that substance. Many experiments were of course required to determine the proportions in which it was advisable to employ the conducting constituent, so as to facilitate the passage of the current through the mass as far as possible, without interfering too much with the sensitiveness of the explosive mixture, or producing an almost perfectly continuous connection between the two poles in the fuze, and thus promoting the passage of the current so greatly as to prevent the ignition of the composition.

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